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THE THERMAL STABILITY OF COBALT AND NICKEL HALIDES

S. A. Shchukarev, T. A. Tolmacheva, and M. A. Oranskaya

An examination of the halides of the Fe, Co and Ni triad shows that, in the case of iron, compounds have been prepared with fluorine, chlorine, and iodine corresponding to valencies of both two and three; in the transition to cobalt and then to nickel, the lower valency, two, becomes increasingly prominent. In the case of cobalt the compound CoF_3 is also known (prepared by the action of fluorine on the difluoride or on metallic cobalt, stable in the solid, liquid, and gas states) and also CoCl_3 which was apparently prepared in 1952 by Schäfer and Krehl [1] in the form of a gas by passing a current of chlorine over CoCl_2 at temperatures above 645° ; it was shown that the amount of cobalt carried over by the gas stream was greater than would correspond to the vapor pressure of CoCl_2 . Schäfer and Krehl tentatively attribute the formula CoCl_3 to the compound, and give the value of the equilibrium constant $K = \frac{P^2 \text{CoCl}_3}{P^2 \text{CoCl}_2 \cdot P \text{Cl}_2}$ in the temperature range $645-800^\circ \text{C}$.

The bromides and iodides of cobalt known at present correspond to the bivalent state of oxidation only.

In the case of nickel the NiX_3 compounds are still less stable, and even NiF_3 has not yet been obtained. Only compounds of the type NiX_2 are known for all the four nickel halides.

In a search for a solution to the problem of valency decrease in the transition from iron to nickel, we made a comparative study of certain thermodynamic data for cobalt and nickel chlorides and bromides*, namely the thermal dissociation pressures of these halides and the values of the free energy, enthalpy, and entropy of their formation.

As the dissociation pressure of the compounds studied is very low, its direct determination is difficult and it is more conveniently determined by an indirect method, for example by the study of some reaction which involves the given halide. We used the reduction of the compounds by hydrogen, so that the reaction equilibrium



was studied.

This is a suitable choice, as the pressure of the halogen in the thermal dissociation of the halides studied is less than the pressure of the halogen which corresponds to the thermal dissociation of the corresponding hydrogen halide; otherwise hydrogen would completely reduce the halide, and the reaction would be practically irreversible**, so that the equilibrium constant could not be determined.

From the values of the equilibrium constants for the given reaction taken in conjunction with the values of the equilibrium constants for the formation of the corresponding hydrogen halide from hydrogen and the halogen, it is possible to find the value of the dissociation pressure of the halide in the metal and the halogen.

The same cobalt and nickel compounds, were already investigated before this in the same way as the studies of the equilibrium of the hydrogen reduction reaction by Jellinek and Uloth [2] (CoCl_2 , CoBr_2 , NiCl_2 and NiBr_2 by the dynamic method, 1926), by Berger and Crut [3] (NiCl_2 by the static method, 1921), by Crut [4] (NiBr_2 , CoCl_2 , CoBr_2 by the static method, 1924), and by Partington and Towndrow [5] (CoCl_2 by the static method, 1924). The data obtained by these authors were used to calculate the standard thermodynamic constants given in Britske and

* Preliminary data on CoCl_2 and CoBr_2 were published in the Bulletin of the Leningrad State University, No. 26 (1950). These results are extended and amplified in the present paper.

** This is very important, as the literature contains instances when, in equilibrium studies, use was made of the reduction of such compounds by hydrogen which should be reduced practically irreversibly, and the observed gas composition was erroneously taken as the equilibrium value. For example, Jellinek used hydrogen reduction in the case of CuCl_2 and CrCl_3 , and his data are quoted in tables.

Kapustinsky's [6] and Brewer's [7] tables. • However, we wished to repeat and amplify these studies, as the data in the literature are very incomplete. Crut's experiments (with the exception of NiCl_2) were carried out at only two temperatures, and with CoCl_2 only at one, which does not provide a sufficiently reliable basis for investigation of the temperature dependence of the constants. Partington and Towndrow made a fairly detailed investigation of the reduction of CoCl_2 (at 10° intervals) but the whole temperature range covered ($400\text{--}500^\circ$) is narrow. Jellinek's data are available for three temperatures only, and, as will be shown later, these three points are not always in good agreement with each other. In addition, the dynamic method used by Jellinek (and by some other workers) for studying the equilibrium does not appear to be always reliable [9].

EXPERIMENTAL

Method of investigation

The circulation method was used for studying the equilibria. Its principle is, as is known, that the gas repeatedly passes over the substance studied, which is kept in a furnace at a definite temperature. Gas samples are analyzed at intervals and the results are used to determine when equilibrium is set up. The equilibrium was approached from two opposite directions. Agreement between the results was taken as proof that equilibrium had been attained.

The apparatus used for the study is shown diagrammatically in Fig. 1, which shows the arrangement of the separate parts, where a) is the furnace, the temperature of which was kept constant to $\pm 1^\circ$; b) is a piece of porcelain tube (instead of the usual boat) with the substance being reduced; c) is a Pt-Pt/Rh; thermocouple; d) are communicating vessels containing mercury for regulating the pressure in the system and for displacement of gas samples for analysis (usually the experiments were carried out at pressures 30-40 mm above atmospheric); e) is a circulating pump with mercury seals, which let gas through in one direction only; the movable bulb is moved up and down with the aid of a motor; f) is a manometer; g) is a three-way tap for taking gas samples; h) is an absorber for the hydrogen halide, filled with distilled water or with standard alkali solution; i) is a gas buret for measuring the volume of hydrogen; j) are tubes with P_2O_5 ; k) are columns with CaCl_2 and KOH; m) is a hydrogen reservoir; n) is an electrolytic cell; o) is a furnace with platinized asbestos; p) is a three-way tap for filling the system with hydrogen and for connecting it to the vacuum pump.

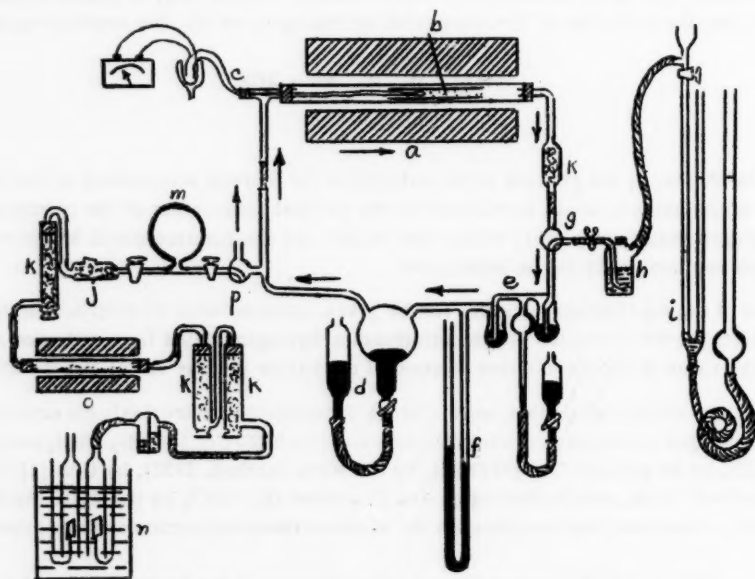


Fig. 1. Scheme of the circulation apparatus used for equilibrium studies.

• After the completion of the present work, a paper was published by Busey and Giauque [8] in 1953, in which the reduction of NiCl_2 by hydrogen is described. The results obtained, as will be shown below, are in close agreement with ours.

When the reaction was conducted from the side of oxidation of the metal by hydrogen halide, excess of the latter in the gas mixture (in comparison with the equilibrium composition) was attained as follows: the substance studied, placed, as usual, in the furnace in a hydrogen atmosphere, was heated to 50-100° above the temperature of the experiment, with the pump working. When the desired composition of gas was reached, the temperature of the furnace was quickly lowered to the required level. In some experiments, if sufficient volume of gas still remained, after an experiment had been carried out at some temperature, the experiment was simply performed at a lower temperature. The total gas pressure in the system and the partial volumes of the two gases in the mixture (from analytical data) were used to calculate the partial pressure of each gas and the value of $\frac{P_{HX}^2}{P_{H_2}}$. After two consecutive samples taken at adequate time intervals gave equal results, the equilibrium could be considered as established; then the ratio $\frac{P_{HX}^2}{P_{H_2}}$ is equal to K_p .

TABLE 1

Substance	Vapor pressure at temperature (°C)		
	10 ⁻⁴ atm. (0.076 mm)	10 ⁻³ atm. (0.76 mm)	10 ⁻² atm. (7.6 mm)
CoCl ₂	507	612	672
CoBr ₂	447	—	—
NiCl ₂	589	661	748
NiBr ₂	487	—	—

The value of the partial pressure of the halogen vapor can be neglected in calculations of the equilibrium constants in the present instance, as this value is negligibly small. According to Brewer's [7] approximate data, the vapor pressure has the values shown in Table 1.

According to Schäfer and Krehl [1], the vapor pressure for CoCl₂ is 0.64 mm at 652° and 4.4 mm at 707°.

Preparation of the samples.

Anhydrous NiCl₂ was prepared by decomposition of the hexamine (NiCl₂ · 6NH₃) which was precipitated from a saturated nickel sulfate solution by an ammonia solution saturated with ammonium chloride. The washed and dried hexamine was heated for a long time at 200° for complete removal of ammonia [10].

Anhydrous NiBr₂ was prepared from nickel carbonate (which, according to spectrographic data, contained not more than 0.001% cobalt) by the action of hydrobromic acid. After evaporation and vacuum drying, the salt was dried in a stream of hydrogen mixed with hydrogen bromide at ~250° C. Analysis showed that the resulting substance contained from 1.5 to 2.5% metallic nickel, formed by reduction with hydrogen, but for our purposes this was unimportant.

Anhydrous CoCl₂ was prepared from commercial CoCl₂ · 6H₂O (chemically pure) by first drying it simply by heating in air, and then (when the nearly anhydrous salt became pale blue) in a stream of dry hydrogen chloride of about 250°.

Anhydrous CoBr₂ was prepared in the same way as nickel bromide, from cobalt carbonate (chemically pure).

As cobalt salts are extremely hygroscopic and could again absorb some moisture during transfer to the furnace, they must be finally dried in the apparatus itself by heating in a vacuum with the pump working.

The purity of all the original nickel and cobalt salts was previously checked by spectrum analysis*.

The equilibria in the reduction of NiCl₂, NiBr₂, CoCl₂ and CoBr₂ by hydrogen were mainly studied in the 300-600° temperature range. The upper limit of this range was sometimes determined by noticeable sublimation of the salt into a less hot part of the furnace, while the remaining salt was often completely, or nearly completely,

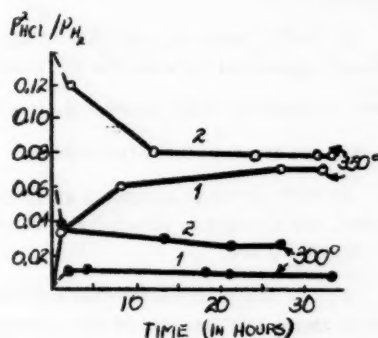


Fig. 2. Variation of gas composition with time (during approach to equilibrium) for the reaction $NiCl_2 + H_2 \rightleftharpoons Ni + 2HCl$
1) Direct reaction, 2) reverse reaction.

* The spectrum analysis was performed by M. M. Kler.

reduced to the metal; in such cases erroneous values of K_p were obtained and often the hydrogen halide content in the samples fell appreciably. This was found, for example, at 655° for NiBr_2 , and at 600° and especially at 700° for CoBr_2 , when no equilibrium was attained at all. Sometimes the limits of the temperature range were determined by the composition of the gas at equilibrium; if the content of one of the gases is only a few percent of the total gas mixture, then a small error in analysis leads to a large error in the value of $\frac{P_{\text{HX}}^2}{P_{\text{H}_2}}$. The lower limit of the temperature range, apart from the reason given, was usually determined by the kinetics of the process. Below 300° the reaction rate was usually so low that although the reaction still proceeded, the process did not reach equilibrium.

The equilibrium in the reduction of nickel chloride by hydrogen was studied * at 300, 350, 420, 450, 470, 500 and 550° C.

At 300° C, with the equilibrium approached from two opposite directions, despite the long time used (up to 33 hours) agreement between the gas phase compositions could not be reached (see Fig. 2). The values found for $\frac{P_{\text{HX}}^2}{P_{\text{H}_2}}$ lie between 0.011 and 0.028 (as will be seen later, the true value of the equilibrium constant is apparently nearer to the lower of these two values).

At 350°, although complete agreement between the results during the approach to equilibrium again was not reached, the divergence between the curves was already much less (Fig. 2) and the average value taken was $K_p = 0.078 \pm 0.004$.

At 420° the reaction reached equilibrium in 6-10 hours. The experiments with nickel chloride were not carried out above 550° because of the unfavorable gas composition ratio and of the appreciable sublimation of the salt.

Table 2 shows all the experimentally determined and assumed values (average, or chosen from the course of the lines in the graphs) for K_p and the volume composition of the gas at equilibrium. * *

The results of the investigation of equilibria in the reduction of NiBr_2 , CoCl_2 , and CoBr_2 are shown in Tables 3, 4 and 5.

DISCUSSION OF RESULTS

An examination of the values obtained for K_p shows that the chlorides of cobalt and nickel are more easily reduced by hydrogen than the bromides (the values of K_p are higher for the chlorides, and appreciable reduction begins at lower temperatures) despite the high thermal stability of the chlorides and the fact that the entropy increase during the reduction is rather less for the chlorides than for the bromides. This is generally true for the great majority of chlorides and bromides and is explained by the much greater heat of formation of HCl in comparison with HBr , which makes the reduction of chlorides less endothermic than that of bromides.

A comparison of Co and Ni compounds with the same halogen shows that cobalt chloride and bromide are more difficult to reduce by hydrogen than the nickel compounds, although the difference in their heats of formation is very small (it is a little greater for cobalt than for nickel halides), and therefore there is little difference in the heat effects of their reduction reactions. Differences in the entropies of cobalt and nickel halides are decisive here.

No heat capacity data (with the exception of NiCl_2 [11]) are available for exact calculations of the thermodynamic functions of the compounds studied, and therefore the usual approximate calculation method was used, which, nevertheless, gives a comparative picture on the basis of which certain conclusions in relation to the periodic system may be drawn.

The values of the equilibrium constants for the reduction of halides by hydrogen were used to calculate, by means of the formula $\Delta F = -RT \ln K_p$, the values for the changes of free energy during the reactions, shown in Tables 2-5. When $\log K_p$ is plotted against $1/T$, the values of $\log K_p$ lie almost exactly on straight lines (this sometimes formed the basis of acceptance for the values of K_p if the experimental results fluctuated) (Figs. 3 and 4).

* With the participation of K. S. Kasimov.

** The arrows \uparrow and \downarrow indicate the direction of the reaction during the approach to equilibrium. The sign \uparrow represents the reaction $\text{MeX}_2 + \text{H}_2 = \text{Me} + 2\text{HX}$, and the sign \downarrow , the reaction $\text{Me} + 2\text{HX} = \text{MeX}_2 + \text{H}_2$. The data in brackets cannot be considered as sufficiently accurate.

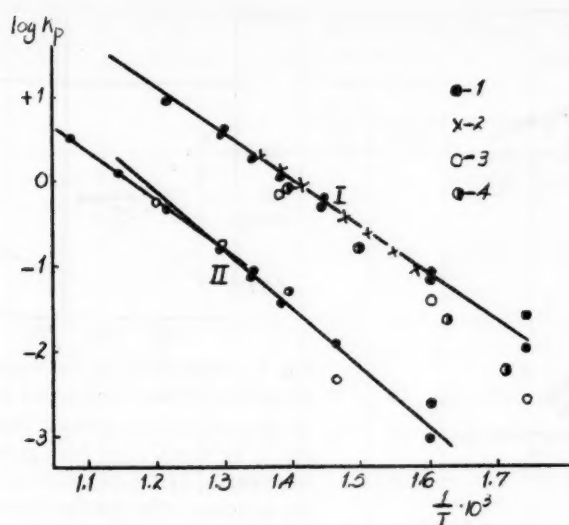


Fig. 3. Dependence of $\log K_p$ on $\frac{1}{T}$ for the reduction of nickel chloride and bromide by hydrogen.

I) $\text{NiCl}_2 + \text{H}_2 \rightleftharpoons \text{Ni} + 2\text{HCl}$, II) $\text{NiBr}_2 + \text{H}_2 \rightleftharpoons \text{Ni} + 2\text{HBr}$.
1) Our data, 2) Busey and Giaque, 3) Jellinek et al, 4) Crut.

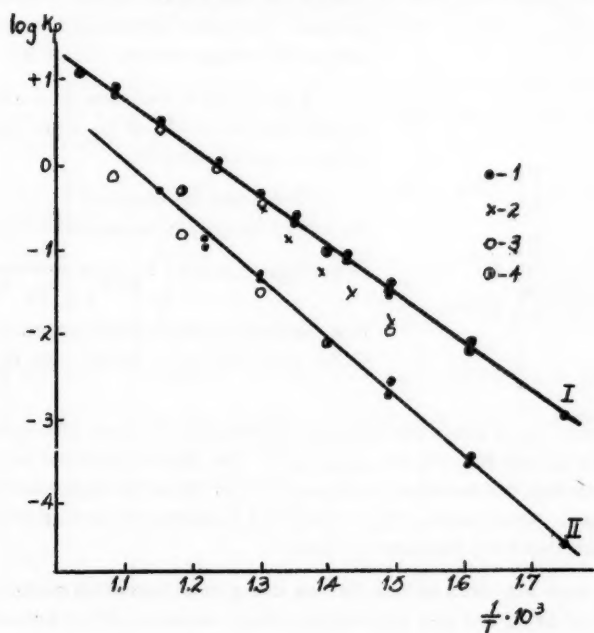


Fig. 4. Dependence of $\log K_p$ on $\frac{1}{T}$ for the reduction of cobalt chloride and bromide by hydrogen.

I) $\text{CoCl}_2 + \text{H}_2 \rightleftharpoons \text{Co} + 2\text{HCl}$, II) $\text{CoBr}_2 + \text{H}_2 \rightleftharpoons \text{Co} + 2\text{HBr}$.
1) Our data, 2) Partington, 3) Jellinek et al., 4) Crut.

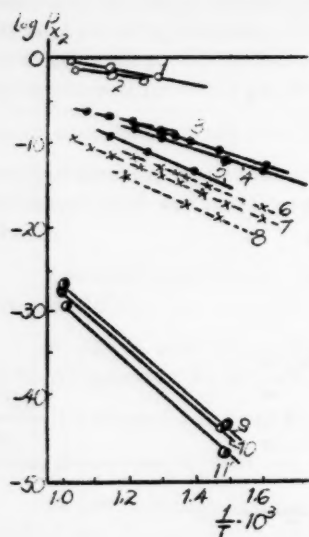


Fig. 5. Dependence of $\log P_{X_2}$ on $1/T$ for the halides of iron, cobalt, and nickel.

- 1) NiI_2 , 2) CoI_2 , 3) NiBr_2 , 4) CoBr_2 ,
5) FeBr_2 , 6) NiCl_2 , 7) CoCl_2 , 8) FeCl_2 ,
9) NiF_2 , 10) CoF_2 , 11) FeF_2 .



Fig. 7. Factors which determine the enthalpy of formation of Fe, Co, and Ni dichlorides.

- 1) ΣI , 2) $\Sigma I + s$, 3) $E + \text{const.}$

For comparison, the same Fig. 5 shows the dissociation pressures of cobalt and nickel fluorides and iodides from the data of Jellinek and Uloth [2] and Jellinek and Rudat [12]. The possibility is not excluded that these results are incorrect for iodides, as the authors did not take the dissociation of HI at the experimental temperature into account, but no other data are available. Nevertheless, Fig. 5 presents a comparative picture of the variation of the thermal stability of halides in the transition from fluorides to iodides.

The values of $\log P_{X_2}$ were also used to find the free energies of formation of the corresponding halides, and then the approximate values of ΔF_{298} and also approximate mean values of ΔH of formation and ΔS of formation for the temperature range studied. The values obtained are shown in Table 6.

It may be seen by an examination of the experimental results that nickel bromide at a little above 500° shows a small break in the $\log K_p$ line and correspondingly in the $\log P_{\text{Br}_2}$ line. Although the equilibrium data at these temperatures are less reliable, it was still reasonable to assume that this effect is explained by a transition to another modification. To verify this assumption, x-ray photographs were taken of nickel bromide specimens; 1) dried in a vacuum at 250° , and 2) held in a vacuum (for 5-6 hours) at $\sim 600^\circ$. Chemical analysis gave the same results for both specimens, corresponding to the composition NiBr_2 . The x-ray diagrams confirmed the existence of different structures.

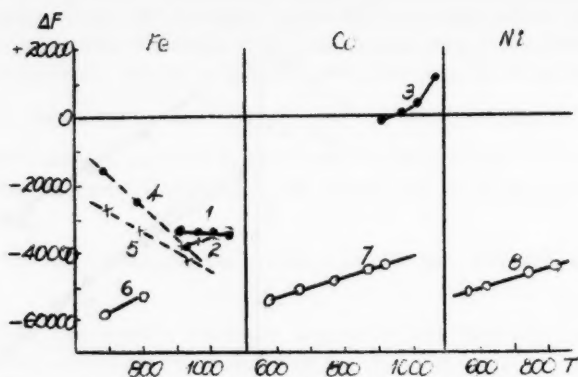


Fig. 6. Dependence of the values of ΔF on temperature for the formation of iron, cobalt, and nickel chlorides.

- 1) FeCl_3 (gas) from gaseous FeCl_2 , 2) Fe_2Cl_6 (gas) from gaseous FeCl_2 , 3) CoCl_3 (gas) from gaseous CoCl_2 , 4) FeCl_3 (gas) from solid FeCl_2 , 5) Fe_2Cl_6 (gas) from solid FeCl_2 , 6) FeCl_2 (s) (from the elements), 7) CoCl_2 (s) (from the elements), 8) NiCl_2 (s) (from the elements).

Because of the linear nature of this relationship, it was assumed as an approximation that, in the temperature range investigated, the entropy (ΔS) and enthalpy (ΔH) values for the reactions are independent of the temperature, and the mean values of these were hence determined for the reduction reaction in the temperature range studied (Table 6).

Figs. 3 and 4 also show data obtained by other authors. It is seen that the results of our experiments agree closely with those of Busey and Giauque [8].

The accepted values of K_p (for the reduction reaction) and the known values for the equilibrium constants for the formation of hydrogen halides ($K_{\text{pHX}} = \frac{P_{\text{HX}}}{P_{\text{H}_2} \cdot P_{\text{X}_2}}$) were used to calculate the thermal dissociation pressures of NiCl_2 , NiBr_2 , CoCl_2 and CoBr_2 , since $\log P_{X_2} = \log K_p - \log K_{\text{pHX}}$ (Fig. 5 and Tables 2-5).

TABLE 2
Nickel chloride

Temperature		$\frac{1}{T} \cdot 10^3$	K_p (experimental)	$\log K_p$	Accepted values		Approximate volume at equilibrium		$\Delta F_{red.}$	P_{Cl_2} (in atm.)	$\log P_{Cl_2}$	$\Delta F_{form.}$ (in cal.)
°C	°K				K_p	$\log K_p$	(in %)					
							H ₂	HCl				
300	573	1.745	$\left\{ \begin{array}{l} 0.028 \downarrow \\ 0.011 \uparrow \end{array} \right.$	$\left\{ \begin{array}{l} -1.55 \\ -1.96 \end{array} \right.$	$\left\{ \begin{array}{l} (0.013) \\ (-1.88) \end{array} \right.$	91	9	+ 4929	$2.6 \cdot 10^{-20}$	-19.59	-51360	
350	623	1.605	$\left\{ \begin{array}{l} 0.082 \downarrow \\ 0.073 \uparrow \end{array} \right.$	$\left\{ \begin{array}{l} -1.09 \\ -1.14 \end{array} \right.$	$\left\{ \begin{array}{l} 0.078 \pm \\ \pm 0.005 \end{array} \right.$	-1.11	76	24	+ 3163	$3.4 \cdot 10^{-18}$	-17.47	-49780
420	693	1.443	$\left\{ \begin{array}{l} 0.58 \downarrow \\ 0.60 \uparrow \end{array} \right.$	$\left\{ \begin{array}{l} -0.24 \\ -0.22 \end{array} \right.$	$\left\{ \begin{array}{l} 0.59 \pm \\ \pm 0.01 \end{array} \right.$	-0.23	47	53	+ 697	$1.0 \cdot 10^{-15}$	-15.00	-47530
450	723	1.383	1.23 ↑	+ 0.09	1.23	+ 0.09	39	61	- 330	$8.0 \cdot 10^{-15}$	-14.10	-46630
470	743	1.346	2.00 ↑	+ 0.30	2.00	+ 0.30	27	73	-1020	$2.8 \cdot 10^{-14}$	-13.55	-46060
500	773	1.293	$\left\{ \begin{array}{l} 4.04 \uparrow \\ 3.9 \downarrow \end{array} \right.$	$\left\{ \begin{array}{l} + 0.61 \\ + 0.59 \end{array} \right.$	$\left\{ \begin{array}{l} 4.00 \pm \\ \pm 0.07 \end{array} \right.$	+ 0.60	18	82	-2129	$1.8 \cdot 10^{-13}$	-12.74	-45060
550	823	1.215	(9.8)	(+ 0.99)	(9.8)	(+ 0.99)	9	91	(-3703)	$(2 \cdot 10^{-12})$	(-11.71)	(-44170)

TABLE 3
Nickel bromide

Temperature		$\frac{1}{T} \cdot 10^3$	K_p (experi- mental)	$\log K_p$	Accepted values		$\Delta F_{red.}$	P_{Br_2} (in atm.)	$\log P_{Br_2}$	$\Delta F_{form.}$ (in cal.)
°C	°K				K_p	$\log K_p$				
350	623	1.605	$\left\{ \begin{array}{l} (0.0016 \downarrow) \\ (0.00098 \uparrow) \end{array} \right.$	$\left\{ \begin{array}{l} (-2.6) \\ (-3.04) \end{array} \right.$	$\left\{ \begin{array}{l} (0.0012) \\ (-2.92) \end{array} \right.$		+ 8324	$3.0 \cdot 10^{-13}$	-12.52	-35690
410	683	1.463	$\left\{ \begin{array}{l} 0.0115 \uparrow \\ 0.0117 \downarrow \end{array} \right.$	$\left\{ \begin{array}{l} -1.94 \\ -1.93 \end{array} \right.$	$\left\{ \begin{array}{l} 0.0116 \pm \\ \pm 0.0001 \end{array} \right.$	-1.94	+ 6061	$1.6 \cdot 10^{-11}$	-10.79	-33720
450	723	1.383	0.040	-1.40	0.04	-1.40	+ 4630	$1.5 \cdot 10^{-10}$	- 9.81	-32450
475	748	1.335	$\left\{ \begin{array}{l} 0.088 \uparrow \\ 0.084 \downarrow \end{array} \right.$	$\left\{ \begin{array}{l} -1.06 \\ -1.08 \end{array} \right.$	$\left\{ \begin{array}{l} 0.084 \pm \\ \pm 0.004 \end{array} \right.$	-1.08	+ 3696	$5.7 \cdot 10^{-10}$	- 9.24	-31550
500	773	1.294	0.165 \uparrow	-0.78	0.165	-0.78	+ 2758	$1.9 \cdot 10^{-9}$	- 8.71	-30800
550	823	1.215	$\left\{ \begin{array}{l} 0.50 \uparrow \\ 0.51 \downarrow \end{array} \right.$	$\left\{ \begin{array}{l} -0.30 \\ -0.29 \end{array} \right.$	$\left\{ \begin{array}{l} 0.50 \pm \\ \pm 0.01 \end{array} \right.$	-0.30	+ 1129	$1.6 \cdot 10^{-8}$	- 7.80	-29370
600	873	1.146	$\left\{ \begin{array}{l} 1.33 \downarrow \\ 1.32 \uparrow \end{array} \right.$	$\left\{ \begin{array}{l} + 0.12 \\ + 0.12 \end{array} \right.$	$\left\{ \begin{array}{l} 1.33 \pm \\ \pm 0.01 \end{array} \right.$	+ 0.12	- 479	$9.8 \cdot 10^{-8}$	- 7.01	-28000
655	928	1.077	$\left\{ \begin{array}{l} (3.1) \uparrow \\ (2.84) \uparrow \end{array} \right.$	$\left\{ \begin{array}{l} (+ 0.49) \\ (+ 0.45) \end{array} \right.$	$\left\{ \begin{array}{l} (3.1) \\ (0.49) \end{array} \right.$		-2080	$5.4 \cdot 10^{-7}$	- 6.27	-26620

The changes in the slopes of the $\log K / \frac{1}{T}$ and $\log P_{Br_2} / \frac{1}{T}$ lines were used to calculate the value of the enthalpy for the transition from one modification to the other; this was found to be about 5.8 kcal. The transition temperature was not determined exactly, but according to the graph it is $\sim 520^\circ C$.

An exactly similar investigation was carried out with cobalt bromide. Here the x-ray diagrams were the same, so that there was no structural change.

TABLE 4

Cobalt chloride

Temperature °C	°K	$\frac{1}{T} \cdot 10^3$	K_p (experimental)	log K_p	Accepted values		$\Delta F_{red.}$	P_{Cl_2} (in atm.)	log P_{Cl_2}	$\Delta F_{form.}$ (in cal.)
					K_p	log K_p				
300	573	1.745	(0.0012) 0.0071	(-2.93) -2.15	(0.0011)	(-2.95)	+7734	$2.2 \cdot 10^{-21}$	-20.66	-54180
350	623	1.605	0.0066 0.0076	-2.18 -2.12	$\frac{0.0069 +}{+ 0.0007}$	-2.16	+6158	$3.0 \cdot 10^{-19}$	-18.52	-52730
400	673	1.486	0.035 ↑ 0.036 ↑ 0.030 ↓	-1.45 -1.44 -1.52	$\frac{0.034 +}{+ 0.004}$	-1.47	+4495	$2.1 \cdot 10^{-17}$	-16.67	-51300
430	703	1.422	0.085 ↓ 0.083 ↑ 0.079 ↓ 0.075 ↑	-1.07 -1.08 -1.10 -1.12	$\frac{0.081 +}{+ 0.004}$	-1.09	+3505	$2.0 \cdot 10^{-16}$	-15.70	-50510
470	743	1.346	0.21 ↓ 0.21 ↑ 0.22 ↑ 0.24 ↓	-0.67 -0.67 -0.66 -0.62	$\frac{0.21 +}{+ 0.02}$	-0.67	+2278	$3.2 \cdot 10^{-15}$	-14.50	-49330
500	773	1.294	0.42 ↓ 0.44 ↑ 0.45 ↑	-0.37 -0.36 -0.34	$\frac{0.44 +}{+ 0.02}$	-0.36	+1273	$2.0 \cdot 10^{-14}$	-13.70	-48450
540	813	1.230	1.00 ↑ 1.07 ↑ 3.2	0.00 +0.03 +0.5	$\frac{1.03 +}{+ 0.04}$	+0.01	-37	$2.0 \cdot 10^{-13}$	-12.69	-47210
600	873	1.147	(7.73)	+0.89	3.2	+0.5	-1997	$4.0 \cdot 10^{-12}$	-11.40	-45530
650	923	1.083	(6.8)	(+1.12)	(7.3)	(+0.86)	(-3632)	$(3.7 \cdot 10^{-11})$	(-10.43)	-44030
700	973	1.028	(13.1)		~ 13	(+1.12)	(~ -4885)	$(2.3 \cdot 10^{-10})$	(- 9.63)	

TABLE 5

Cobalt bromide

Temperature °C	Temperature °K	$\frac{1}{T} \cdot 10^{-3}$	K_p (experimental)	log K_p	Accepted values		$\Delta F_{\text{red.}}$	P_{Br_2} (in atm.)	log P_{Br_2}	$\Delta F_{\text{form.}}$ (in cal.)
					K_p	log K_p				
300	573	1.745	(0.000007)	(-5.29)	{ ~0.00003 }	{ ~-4.5 }	-	-	-	-
			(0.000003)	(-4.52)						
			(0.000009)	(-4.03)						
350	623	1.605	0.00033 ↓	-3.49	{ 0.00032 + +0.00002 }	-3.5	+9977	$7.9 \cdot 10^{-14}$	-13.10	-37350
			0.00031 ↑	-3.51						
			0.00028 ↓	-3.55						
400	673	1.485	0.0026 ↓	-2.58	{ 0.0021 + +0.0004 }	-2.67	+8221	$2.3 \cdot 10^{-12}$	-11.63	-35810
			0.0019 ↓	-2.72						
			0.047 ↓	-1.33						
500	773	1.294	0.047 ↑	-1.33	{ 0.047 + +0.001 }	-1.33	+4704	$5.4 \cdot 10^{-10}$	-9.26	-32750
			0.044 ↑	-1.36						
			0.11	-0.96						
550	823	1.215	0.12	-0.92	(0.16)	(-0.8)	+3012	($5.0 \cdot 10^{-9}$)	(-8.3)	(-31250)
600	873	1.147	(0.50) ↑	(-0.3)	(0.5)	(-0.3)				

TABLE 6

Substance	T (° K)	MeX ₂ + H ₂ = Me + 2HX		Me + X ₂ = MeX ₂		
		ΔH _{red.} (in kcal.)	ΔS _{red.} (in entropy units)	ΔH _{form.} (in kcal.)	ΔS _{form.} (in entropy units)	ΔF ₂₉₈ (in kcal.)
NiCl ₂	573-823	+ 25.14	+ 35.2	-69.5	-31.5	-60.01
NiBr ₂	623-790	+ 31.14	+ 36.7	-55.84	-32.45	-46.20
NiBr ₂	790-928	-	-	~-50	-	-
CoCl ₂	573-743	+ 26.44	+ 32.6	-71.0	-29	-62.34
CoBr ₂	573-873	+ 31.88	+ 35.15	-56.4	-30.6	-47.31

TABLE 7

Reaction	ΔS for the reaction
2FeCl ₂ (S) + Cl ₂ + 46.2 kcal. = 2FeCl ₃ (gas)	+ 90
2FeCl ₂ (S) + Cl ₂ + 13.6 kcal. = Fe ₂ Cl ₆ (gas)	+ 59
2FeCl ₂ (gas) + Cl ₂ - 29.8 kcal. = 2FeCl ₃ (gas)	+ 4.8
2FeCl ₂ (gas) + Cl ₂ - 62.4 kcal. = Fe ₂ Cl ₆ (gas)	- 26.4
2CoCl ₂ (gas) + Cl ₂ - 33.8 kcal. = 2CoCl ₃ (gas)	- 36.3

TABLE 8

Temperature ° K	ΔF (in cal.)		
	2FeCl ₂ (gas) + Cl ₂ = = Fe ₂ Cl ₆ (gas)	2FeCl ₂ (gas) + Cl ₂ = = 2FeCl ₃ (gas)	2CoCl ₂ (gas) + Cl ₂ = = 2CoCl ₃ (gas)
918	-38100	-34210	- 631
971	-36700	-34460	+ 1191
1019	-35300	-34680	+ 3477
1073	-33970	-34950	+ 11420

TABLE 9

Temperature ° K	ΔF (in cal.)	
	2FeCl ₂ (s) + Cl ₂ = FeCl ₄ (gas)	2FeCl ₂ (s) + Cl ₂ = 2FeCl ₃ (gas)
700	-27700	-16800
800	-33600	-25800
940	-41840	-38400

TABLE 10

Element	s	ΣI	ΣI + s	The difference ΣI + s for adjacent elements	E for MeCl ₂	Difference of E for adjacent elements	E + const.	ΔH
Fe	96.7	545.8	642.5	23.7	607.5	13.5	724.5	82
Co	85	581.2	666.2	28	621	26.6	738	72
Ni	85	609	694		647.6		764.6	70.6

Our mean values for the enthalpy of formation could only be used in the case of NiCl_2 to find ΔH_{298} , as the necessary heat capacity data are available in that instance. For NiCl_2 Coughlin's [11] data were used, and for Ni, the specific heat equations:

$$C_p = 4.26 + 6.40 \cdot 10^{-3} T \quad (273-626^\circ \text{K}),$$

$$C_p = 6.99 + 0.905 \cdot 10^{-3} T \quad (626-1725^\circ \text{K}) [6],$$

the heat of transition of nickel was taken as 92 cal.; for chlorine, the data of Glaue and Overstreet [6] were used.

Recalculation of our mean value of ΔH from 700° K (the middle of the temperature range studied) to 298° K gave the value $\Delta H_{298} = 70.5 \text{ kcal.}$

Comparison of iron, cobalt, and nickel halides

In conclusion, it was of interest to make some comparisons between the iron, cobalt, and nickel compounds with the use of our results and of the data available in the literature.

For a comparison of the probability of formation of trivalent iron, cobalt, and nickel halides we will confine ourselves to an examination of the chlorides. The fact that the compounds CoCl_3 and NiCl_3 cannot be expected to be stable can be concluded in advance from an examination of the values of the third ionization potentials of Fe, Co, and Ni.

As was shown by Shchukarev and Oranskaya [13], the values of the dissociation pressures of halides during consecutive transition from one element to another (for the elements of the first sub-period) change symbatically with the values of the ionization potentials, and in the present instance with the value of the third ionization potential, since the reaction $2\text{MeCl}_3 \rightleftharpoons 2\text{MeCl}_2 + \text{Cl}_2$ is involved. These have the following values [14].

	Mn	Fe	Co	Ni
$I_3 \text{ kcal/g-atom}$	782	727	772	825

For solid FeCl_3 , according to Kangro and Petersen [15] the dissociation pressure at 300° is about 50 mm. Solid CoCl_3 should be less stable, and its stability should be near to that of MnCl_3 (Co and Mn have similar values of I_3), and NiCl_3 is obviously still less stable. So far these compounds have not been obtained in the solid state. The formation of CoCl_3 and MnCl_3 in the gaseous state was detected by the action of excess chlorine on MeCl_2 vapors. Ferric chloride is stable both in the solid and in the gaseous states, and the gaseous state is represented by the equilibrium:



The equilibrium constants for this reaction were calculated by Schäfer [16] by an indirect method and later determined by Kangro and Bernstorff [17] by a static method in the temperature range 487-741° C. Their results show that at lower temperatures dimer molecules predominate, and as the temperature rises the equilibrium shifts in the direction of the monomer (at a total pressure of 100 mm and at ~800° C almost complete decomposition into the monomer takes place).

To determine the probability of reactions leading to the formation of trivalent Co and Ni halides, an attempt was made to compare the values of the free energy of the reactions of formation of these compounds, that is, for the reactions:



For the chlorides of iron, the data of Schäfer [18] and of Kangro and Bernstorff [17] were used, and for cobalt chloride, the data of Schäfer and Krehl [1], to calculate the values of ΔF for the reactions shown in Table 7.

The individual entropy values required for the calculation of ΔS for these reactions were taken as (in entropy units): $\text{Fe}_2\text{Cl}_6 (\text{gas})$, 171, from Schäfer [18]; $\text{FeCl}_2 (\text{gas})$, 72.1 from Britske and Kapustinsky [6]; $\text{Cl}_2 (\text{gas})$, 53.3, from Britske and Kapustinsky [6]; $\text{FeCl}_3 (\text{gas})$, 101, our calculation from the data of Kangro and Bernstorff [17] and Schäfer [18]; $\text{FeCl}_2 (\text{s})$, 29.4, from Britske and Kapustinsky [6].

The values of ΔF given in Tables 8 and 9 were calculated on the assumption that ΔH and ΔS for the reactions are independent of temperature in the temperature range considered. For solid FeCl_2 the calculation was made to approximate the melting point of this compound (674°).

For the reactions between gaseous MeCl_2 and chlorine we selected, for convenient comparison, the temperature range for which Schäfer and Krehl's experimental data for CoCl_3 are available; in absence of other data we assumed, like these authors, that CoCl_3 itself and not the dimer is formed (which is not certain at present).

For the reactions of formation of solid MeCl_2 from the metals and chlorine, our data (Tables 2, 4) were used for CoCl_2 and NiCl_2 , and the data of Shchukarev, Oranskaya, and Novikov [19] for FeCl_2 .

The values of ΔF so obtained (Tables 2, 4, 8, and 9) were used to plot the ΔF -temperature curves (Fig. 6). Fig. 6 shows that in the case of iron the values of free energy for the formation both of FeCl_3 (gas) (1) and Fe_2Cl_6 (gas) (2) from gaseous FeCl_2 are far below zero, and the reaction of Fe_2Cl_6 formation is at first the more favorable; at about 770° the curves for these processes intersect.

For CoCl_3 (gas) the Curve (3) lies almost entirely in the region of positive ΔF values. If we assume that not CoCl_3 but the dimer is formed, the position of the curve would, of course, change, but apparently it would remain in the same region. Thus, a comparison of the curves shows that CoCl_3 should be much less stable than FeCl_3 .

The reactions for the formation of FeCl_3 (gas) (4) and Fe_2Cl_6 (gas) (5, Fig. 6) from solid FeCl_2 are endothermic, but as they are accompanied by large entropy increases (and therefore the ΔF curves for these reactions are very steep) at sufficiently high temperatures they can compete with the reactions of gaseous FeCl_2 .

The reaction $2\text{CoCl}_2(s) + \text{Cl}_2 + 76.4 \text{ kcal.} = 2\text{CoCl}_3(\text{gas})$ is highly endothermic, which is due to the high heat of sublimation of CoCl_2 (55 kcal., according to Schäfer and Krehl [1]). For the calculation of the free energy of this reaction, no data are available for the entropy of cobalt chlorides. Tentatively assumed values (by analogy with the iron compounds) give results which are too inaccurate, and are not reproduced here; it appears, however, that the ΔF values lie in the highly positive region (of the order of 20-40 kcal.).

NiCl_3 should be even less stable than CoCl_3 , but its formation may be assumed possible at high pressures of chlorine.

The values of ΔF for the formation of solid FeCl_2 (6), CoCl_2 (7), NiCl_2 (8) all lie far down on the graph, which is in agreement with the stability of these compounds.

The bromides and iodides are as a rule, less stable than the chlorides; therefore they obviously cannot be obtained for trivalent Co and Ni. The formation of NiF_3 may be presumed, although it is still unknown.

In a comparison of Fe, Co, and Ni compounds it is interesting to attempt to find a reason for the great similarity between cobalt and nickel and their difference from iron. If the values of the enthalpy of formation of a large number of binary compounds of these three elements are examined, it is seen that they are always very similar for analogous Co and Ni compounds, and generally differ by less than 2 kcal., while the difference between the enthalpies of formation of iron compounds and the enthalpies of formation of the same cobalt compounds are several kilocalories.

The enthalpy of formation of bivalent metal halides may be given by the following equation:

$$\Delta H = (E + 2e - (D + \Sigma I + s),$$

where E is the lattice energy, e is the halogen electron affinity, D is the dissociation energy of 1 mole of the halogen, ΣI is the sum of the 1st and 2nd dissociation potentials, and s is the energy of sublimation of the metal.

For the same halogen, $2e - D = \text{const}$, and the difference between the values of ΔH for the halides of the three elements in question will depend on the difference $E - (\Sigma I + s)$.

The data in Table 10 for compounds of the type MeCl_2 for Fe, Co, and Ni, show that only the values of the energy of sublimation for Co and Ni are equal [6], and for iron it is somewhat greater, while the other values which determine the value of ΔH are not near each other for cobalt and nickel, and as a result the values of E and $(\Sigma I + s)$ differ even more for Ni and Co than for Co and Fe.

However, the difference between changes in the values of E and the values of $\Sigma I + s$ is almost the same in the transition from cobalt to nickel, which leads to similar values of ΔH , while for iron this difference is not the

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THE ROLE OF IONIZATION POTENTIALS IN THE THERMODYNAMICS OF THE HALIDES OF METALS IN THE FIRST SUB-PERIOD OF THE FOURTH PERIOD OF D. I. MENDELEEV'S SYSTEM

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It is interesting to determine the causes which affect the possibility of the existence of a given element in a particular degree of oxidation. The obvious way of solving the problem is to refer to the periodic law and to compare the thermal stabilities of the compounds of some definite class, for example, the chlorides of the elements of the first sub-period of the fourth period in Mendeleev's system. The reason for the choice of the chlorides of these elements was that the greatest amount of experimental data is available in the literature for them [1]. The dissociation pressure of a compound is taken as a measure of its thermal stability. A compound can exist under normal pressures if its dissociation pressure at a given temperature is less than 1 atm., and the compound decomposes if this pressure exceeds 1 atm.*.

The following chlorides of the first sub-period have been obtained:

-	-	-	-	-	-	-	-	-	-
-	TiCl ₂	VCl ₂	CrCl ₂	MnCl ₂	FeCl ₂	CoCl ₂	NiCl ₂	CuCl ₂	ZnCl ₂
ScCl ₃	TiCl ₃	VCl ₃	CrCl ₃	MnCl ₃	FeCl ₃	CoCl ₃	-	-	-
-	TiCl ₄	VCl ₄	CrCl ₄	-	-	-	-	-	-

We first examine the dihalides. The values for the dissociation pressures of FeCl₂ [2], CoCl₂, NiCl₂ [3] and CuCl₂ were determined [4] by us, those for ZnCl₂ and VCl₂ were calculated from Brewer's tables [1], for CrCl₂ the data of Sano [5] and Doerner [6], and for MnCl₂ the data of Sano [7] were used. Table 1 shows the logarithms of the dissociation pressures of all these compounds (for their dissociation into the metal and chlorine) at various temperatures.

In Fig. 1, the logarithms of the dissociation pressure (at 400°) are taken along the ordinate axis, and calcium and the elements of the first sub-period are plotted along the abscissa axis. It is seen that the dissociation pressure gradually increases with the atomic number, but it has minimum values for MnCl₂ and ZnCl₂. The same figure shows the enthalpies of decomposition for these compounds.** As was to be expected, the enthalpy change from one element to another is antipathetic to the change of the dissociation pressure, so that a low enthalpy of decomposition corresponds to a high dissociation pressure (CuCl₂), and, conversely, a high enthalpy of decomposition corresponds to a low dissociation pressure (TiCl₂, VCl₂, MnCl₂).

The course of the dissociation pressure curve plotted against the atomic number of the element should depend on values which characterize the cation, since the anion remains the same. Such values are, primarily, the sublimation energy of the metal and the first and second ionization potentials. Fig. 2 shows the variations of the sublimation energy (1), and of the first (2) and the second (3) ionization potentials, and of the sum of all these three, (5), with the atomic number of the element. Fig. 2 shows that only the curve for the second ionization potential (3) reproduces the curve for the dissociation pressure, and the resemblance between the curves becomes still more complete if the sum of the two potentials and the sublimation energy is taken (5), but the principal part is still played by the second ionization potential, as the principal term. Consequently, the change in the dissociation pressure, or the change in the thermal stability of the compounds, is in the first instance determined by the value of the second ionization potential. How is such an influence of this particular factor to be explained?

* The possibility of the existence of compounds at high pressures is not considered here.

** The enthalpies are quoted for standard conditions, because specific heats have not been determined for every chloride.

TABLE 1

Temperature °C	Logarithm of dissociation pressure • (log P)								
	TiCl ₂	VCl ₂	CrCl ₂	MnCl ₂	FeCl ₂	CoCl ₂	NiCl ₂	CuCl ₂	ZnCl ₂
219	-	-	-	-	-	-	-	-13.0	-
320	-	-	-	-	-	-	-	-10.2	-
350	-	-	-	-	-	-18.5	-17.5	-	-
392	-	-	-	-	-	-	-	- 8.7	-
400	-32.7	-29.9	-22.9	-29.0	-19.3	-16.7	-15.7	- 8.5	-24.6
420	-	-	-	-	-	-	-15.0	- 8.1	-
423	-	-	-	-	-18.6	-	-	-	-
427	-31.1	-28.7	-	-	-	-	-	-	-23.0
450	-	-	-	-	-	-	-14.1	-	-
470	-	-	-	-	-	-14.5	-13.6	-	-
473	-	-	-	-	-17.1	-	-	-	-
496	-	-	-	-	-16.4	-	-	-	-
500	-	-	-	-	-	-13.7	-12.7	-	-
523	-	-	-	-	-15.6	-	-	-	-
527	-25.7	-24.1	-	-	-	-	-	-	-
540	-	-	-	-	-	-12.7	-	-	-
547	-	-	-	-22.9	-	-	-	-	-
550	-	-	-	-	-	-	-11.7	- 6.0	-
595	-	-	-	-	-13.8**	-	-	-	-
600	-	-	-	-	-	-11.4	-	-	-
627	-22.5	-20.5	-	-20.2	-	-	-	-	-
632	-	-	-16.2	-	-	-	-	-	-
650	-	-	-	-	-	-10.4	-	-	-
677	-	-	-15.2	-	-	-	-	-	-
700	-	-	-	-	-	- 9.6	-	-	-
702	-	-	-	-	-11.9	-	-	-	-
725	-	-	-	-	-11.5	-	-	-	-
727	-19.4	-17.9	-	-	-	-	-	-	-15.3
772	-	-	-13.3	-	-	-	-	-	-
800	-	-	-	-	-10.3	-	-	-	-
805	-	-	-12.7	-	-	-	-	-	-
827	-16.9	-15.6	-	-	-	-	-	-	-13.3
893	-	-	-11.3	-	-	-	-	-	-
925	-	-	-	-	- 9.0	-	-	-	-
1005	-	-	-	-	- 8.1	-	-	-	-
1075	-	-	- 8.7	-	-	-	-	-	-

• The dissociation pressure is in atmospheres throughout.

•• From 595° the dissociation pressure of FeCl₂ was calculated from the data of Sano [7] and Bagdasarian [9].

If we calculate the crystal lattice energies of the compounds in question and plot them on a graph, we again obtain a curve which resembles the curve for the sum of the ionization potentials and the sublimation energy (Table 2, Fig. 3).

In Fig. 3, the Curves 1, 2, 3, show the course of the variation of the lattice energies for the chlorides (1), bromides (2) and iodides (3) of the elements in the first sub-group. • To the lattice energy a value is added which is constant for the given class of compounds, $-D + 2e$, where D is the dissociation energy of the halogen and e is the

• The values of the ionization potentials were taken from [10], and the sublimation energies and enthalpies of formation from [11] and [1]; the enthalpies for the bromides and iodides were calculated for the formation of these compounds from gaseous halogens. The dissociation energies and the halogen electron affinities were taken from [12].

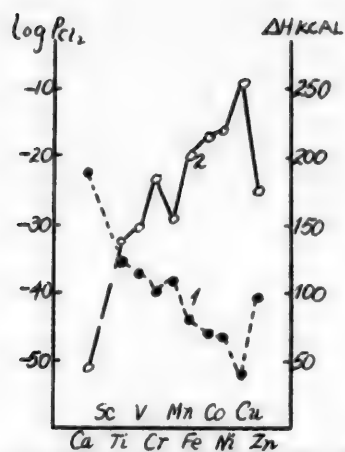


Fig. 1. Variation of the logarithm of the dissociation pressure of chlorides at 400°, and of the enthalpy of dissociation, in consecutive transition from Ca to Zn. 1) Enthalpy of dissociation, 2) logarithm of dissociation pressure.

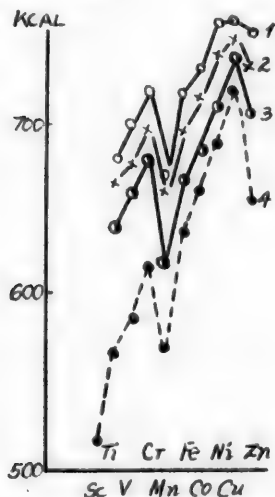


Fig. 3. Comparison of the changes of $E + \text{const.}$ for halides with changes in the sum of the ionization potentials and sublimation energy for the elements of the first sub-period. 1) $E + \text{const.}$ (chlorides), 2) $E + \text{const.}$ (bromides), 3) $E + \text{const.}$ (iodides), 4) $I_1 + I_2 + s$.

halogen electron affinity. • It is seen that the Curves 1, 2, 3 (Fig. 3) follow the course of the ionization potential curve, but their absolute values lie higher and they are flatter than the $\Sigma I + s$ curve (4). Such a resemblance between the curves may be seen not only for the halides of the elements of the first sub-period, but also for the compounds of these elements with the elements

• The significance of adding $-D + 2e$ will be explained later.

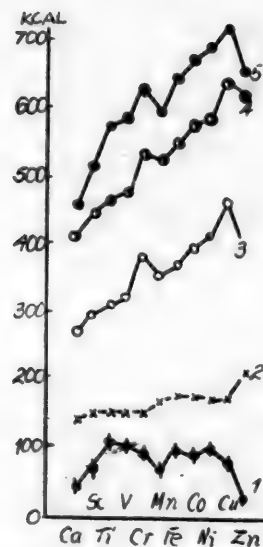


Fig. 2. Variation of the sublimation energy s (1), the first ionization potential I_1 (2), the second ionization potential I_2 (3), the sum of the two potentials $I_1 + I_2$ (4), and the sum of the ionization potentials and the sublimation energy $I_1 + I_2 + s$ (5) in consecutive transition from Ca to Zn.

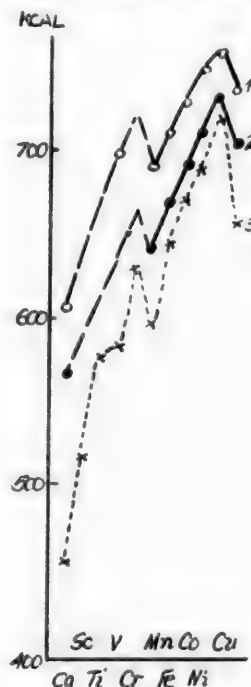


Fig. 4. Comparison of the changes of $E + \text{const.}$ for oxides and sulfides with changes in the sum of the ionization potentials and sublimation energy for the elements of the first sub-period. 1) $E + \text{const.}$ (oxides), 2) $E + \text{const.}$ (sulfides), 3) $I_1 + I_2 + s$.

of the sixth group (Fig. 4), and also for the compounds of the principal sub-groups, for example, the halides of the first group (both the alkali metals, Fig. 5, and the copper sub-group, Fig. 6). Since the course of the curve is not changed by the addition of the constant value, it may be assumed that for analogous compounds the curve for the lattice energy is symbatic with the ionization potential curve (as was stated earlier, the decisive role is played by the ionization potential). This is clearly seen in Figs. 5 and 6, where the lattice energies (1, 2, 3) and the ionization potentials (4) are taken along the ordinate axes. This symbatic nature of the courses of the lattice energy curve and the ionization potential curve may be attributed to a certain resemblance between the processes, as in both cases the positively charged ions of a given metal are combined with negatively charged particles — in the first instance, electrons, and in the second, anions. In Figs. 3 and 4 the constant value $-D + 2e$ is added to E , and s is added to $I_1 + I_2$ in order that the distance between the curves should directly represent the enthalpy of formation.

$$\Delta H = E + \text{const} - (\Sigma I + s).$$

TABLE 2

Element	Sublimation energy \bar{s} (in kcal./g-atom)	Ionization potential (in kcal./g-atom)		$I_1 + I_2$	$I_1 + I_2 + \bar{s}$	Enthalpy of formation ΔH (in kcal./mole)	Lattice energy E_{MeCl_2} (in kcal./mole)
		I_1	I_2				
Se	70	154.1	294.4	448.5	518.5	—	—
Ti	100	156.6	312.8	469.4	569.4	-125*	-577.4
V	85	155	348	503	588	-117	-588
Cr	89.3	154.1	377.4	531.5	620.9	-103.1	-607
Mn	69.7	170.4	333.5	503.9	573.6	-111.6	-568
Fe	96.7	180.1	365.7	545.8	642.5	-82	-607.5
Co	85	179.4	401.8	581.2	666.2	-72	-621
Ni	85	174.8	434.2	609	694	-70.6	-647.6
Cu	81.2	176.4	467.4	644	725.2	-41.2	-649.4
Zn	31.2	215.5	414.9	630.4	661.6	-99.3	-643.9

* There are no experimental data for the heat of formation of TiCl_2 . Brewer assumes it to be -115 kcal. by extrapolation, -125 kcal. seems to us more correct.

In all cases given, the curve for the lattice energy + const. is higher in absolute values, and as a rule is more flat, than the curve for the ionization potentials, from which it follows that as the ionization potential increases, the distance between the curves becomes less, that is, the ΔH of formation decreases, and consequently the dissociation pressure increases. Conversely, as the ionization potential falls, the distance between the curves becomes greater, and therefore the enthalpy of formation increases while the dissociation pressure falls. This explains the symbatic nature of the courses of the dissociation pressure curve and the ionization potential curve. Admittedly, there are some deviations from this in Fig. 3. In some regions portions of the $E + \text{const.}$ curve are steeper than $\Sigma I + \bar{s}$. This is found in the $\text{VI}_2\text{-CrI}_2$ and $\text{CrI}_2\text{-MnI}_2$ regions, which are compounds for which the thermodynamic data have not been determined with sufficient accuracy, and it is possible that after further investigation the deviations from the rule will diminish or even vanish.

It can be shown that during the dissociation of compounds of metals of higher valency than two, for example, in the dissociation of



or



the dissociation pressure will also vary with the third or fourth ionization potential. The dissociation pressures (at 400°) and enthalpies of the dissociation reactions of tri- and tetrachlorides are shown in Tables 3 and 4.

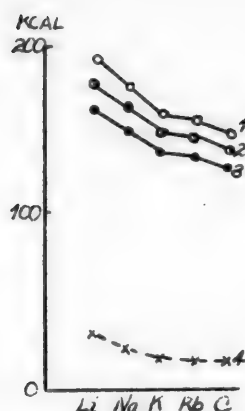


Fig. 5. Comparison of changes in the values of crystal lattice energies of halides with changes in the first ionization potential of alkali metals.

1) E (chlorides), 2) E (bromides), 3) E (iodides), 4) curve for the first ionization potential of the alkali metals.

dissociation potentials, and the abscissa axes give the elements of the first sub-period. It is seen that here, as for MeCl_2 , the dissociation pressure curves and the ionization potential curves are symbatic. The dissociation pressure curve, like the third dissociation potential curve, has a maximum for MnCl_3 and a minimum for FeCl_3 , and the ionization potential then rises. CoCl_3 in the solid state is extremely unstable and was prepared in 1952 by Schäfer and Krehl [14] only in the vapor state by the action of excess chlorine on CoCl_2 at temperatures above 645° . The existence of NiCl_3 , CuCl_3 , and ZnCl_3 is still less probable.

TABLE 3

Substance	I_3 (in kcal./g-atom)	$\log P_{\text{Cl}_2}$	ΔH (in kcal./mole)	Literature source
ScCl_3	618	—	—	—
TiCl_3	652.5	-24.9	+ 100	—
VCl_3	696	-16.1	+ 86	—
CrCl_3	736	-14.5	+ 80	[6]
MnCl_3	782	+ 8.3	- 3	[1]
FeCl_3	727	+ 0.3	+ 28	[13]
CoCl_3	772	—	—	[14]•
(NiCl_3)	825	—	—	—
(CuCl_3)	916	—	—	—
(ZnCl_3)	919	—	—	—

• The data of Schäfer and Krehl [14] are not quite comparable with the data for the other trichlorides, as they prepared gaseous CoCl_3 from gaseous CoCl_2 , while in the other instances the values are given for the dissociation of solid MeCl_3 into the halogen and solid MeCl_2 .

The dissociation of MeCl_4 shows an ascending straight line only. The minimum on the ionization potential curve is found at Co, but Cr, which has a much lower ionization potential than Co, forms the very unstable compound CrCl_4 , which can only be obtained in the solid state below -80°C [15], and therefore compounds of the type MeCl_4 are unlikely in elements beyond chromium.

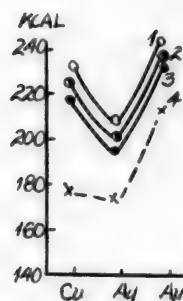


Fig. 6. Comparison of changes in the values of crystal lattice energies of halides with changes in the first ionization potential of copper, silver, and gold.

1) E (chlorides), 2) E (bromides), 3) E (iodides), 4) curve for the first ionization potential of Cu, Ag, and Au.

In Figs. 7 and 8 the ordinate axes show the logarithms of the dissociation pressures of MeCl_3 and MeCl_4 , and also the values of the third and fourth

TABLE 4

Substance	I_4 (in kcal./g-atom)	$\log P_{\text{Cl}_2}$	ΔH (in kcal./mole)	Literature source
ScCl_4	1715	—	—	—
TiCl_4	1043	-10.95	+ 32.8	—
VCl_4	1113	- 2.6	+ 4	—
CrCl_4	1170	+ 11.9	-44	[6]
(MnCl_4)	1230	—	—	—
(FeCl_4)	1288	—	—	—
(CoCl_4)	1223	—	—	—
(NiCl_4)	1290	—	—	—
(CuCl_4)	1350	—	—	—
(ZnCl_4)	1420	—	—	—

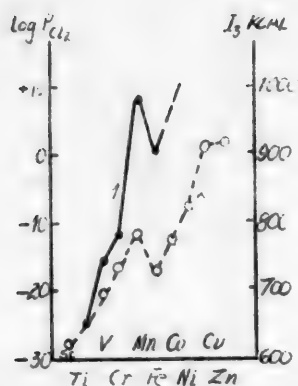


Fig. 7. Variation of the logarithm of the dissociation pressure for the reaction $2\text{MeCl}_3 \rightleftharpoons 2\text{MeCl}_2 + \text{Cl}_2$ at 400°C , and of the third ionization potential in the transition from Sc to Zn.

1) $\log P_{\text{Cl}_2}$, 2) I_3 .

TABLE 5

Halogen	Electron affinity e (kcal./g-atom)	Dissociation energy D (kcal./mole)	$2e-D$
Fluorine	83	40	126
Chlorine	87	57	117
Bromine	81.6	45.2	118
Iodine	74.0	36.3	111.7

the halogen, and its electron affinity. The greater these three values are, the smaller will be the role of the constant subtracted from the lattice energy, the greater will be the enthalpy of formation, and the less will be the dissociation pressure. Table 5 gives the electron affinity and dissociation energy values for the halogens. The electron affinity and the dissociation energy of fluorine were taken as 83 kcal./g-atom and 40 kcal./mole [16].

Thus we see that the value $2e-D$ which is added to the lattice energy is greatest for fluorine, almost the same for chlorine as for bromine, and least for iodine, but these values do not greatly differ from each other (by not more than 14 kcal.). Therefore, the main influence on the value of the enthalpy of formation of the compounds should be exerted by the energy of the crystal lattice, which should increase as its component particles are able to approach closer to each other.

In compounds of the same metal the lattice energy will depend on the size of the halogen atoms. Fluorine will give compounds with the greatest lattice energy, and iodine, the least. The values which characterize the anion, $2e-D$, as was already shown, change in the same direction; therefore the enthalpy of formation will be greatest for fluorides and least for iodides, while the dissociation pressure, which is a measure of the thermal stability of the compounds, will change in the opposite sense (Fig. 9, Table 6).

Fig. 9 shows logarithms of the dissociation pressures of different halides of the elements of the first sub-period at 400° . Parallel to the abscissa axis is a line a , which represents a dissociation pressure of 1 atmosphere. It is seen that while the dissociation pressures of fluorides lie well below the line a , the dissociation pressures increase in the transition to iodides, and for iodides the curves lie near the line a . The normal order of dissociation pressures for compounds of different valencies of the same element is such that compounds of lowest valency have the lowest pressure, and those of the highest valency, the greatest pressure. • Thus fluorides can form compounds in which the

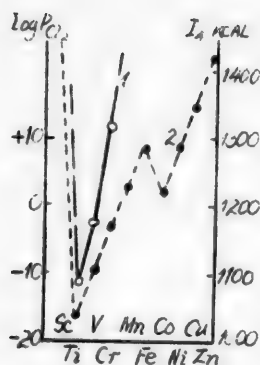


Fig. 8. Variation of the logarithm of the dissociation pressure for the reaction $2\text{MeCl}_4 \rightleftharpoons 2\text{MeCl}_3 + \text{Cl}_2$ at 400°C and of the fourth ionization potential in the transition from Sc to Zn.

1) $\log P_{\text{Cl}_2}$, 2) I_4 .

So far we have examined compounds of metals with the same halogen; if we now compare the thermal stabilities of different halides of the same metal, then we have for such compounds of bivalent metals:

$$\Delta H = E - D + 2e - \Sigma I - s.$$

The last two terms will be constant in the present instance, and the enthalpy of formation will depend on the lattice energy, dissociation energy of

• In the event of a disproportionation reaction the order of pressures is disturbed.

element exhibits its highest valency; in iodides even compounds of the lowest valency are unstable, while compounds of the highest valency cannot exist at 400°, and atmospheric pressure (with the exception of TiI_4).

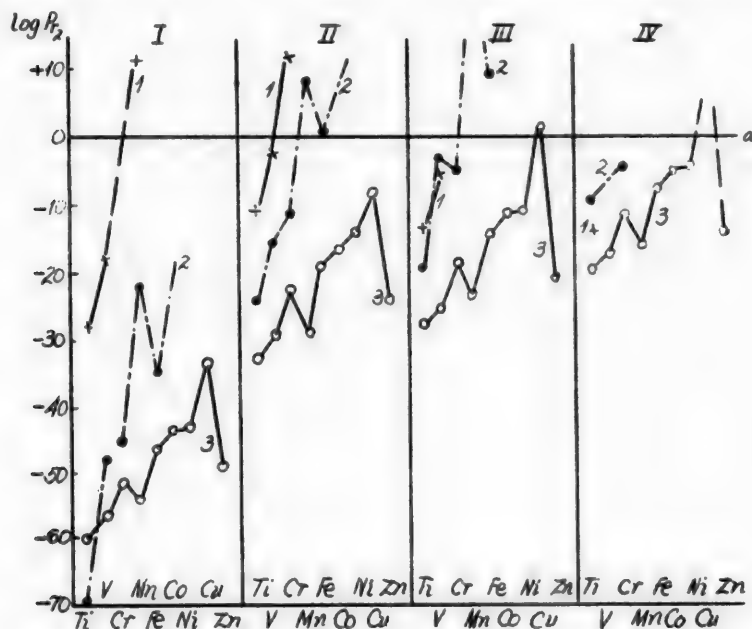


Fig. 9. Variation of the logarithm of the dissociation pressure of halides at 400° in the transition from Ti to Zn.

I) Fluorides, II) chlorides, III) bromides, IV) iodides.

1) $2MeX_4 \rightleftharpoons 2MeX_3 + X_2$, 2) $2MeX_3 \rightleftharpoons 2MeX_2 + X_2$; 3) $MeX_2 \rightleftharpoons Me + X_2$.

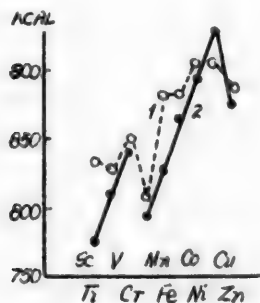
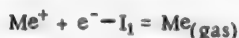
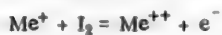
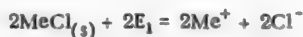


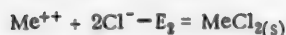
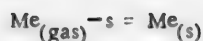
Fig. 10. Enthalpy of disproportionation of $MeCl$ compounds as the distance between the curves $E_2 + s + I_1$ (1) and $2E_1 + I_2$ (2).

On the question of the possible existence of compounds of univalent metals of the first sub-period, it may be concluded that compounds of a given valency cease to exist either because the dissociation pressure of the compound at the given temperature is very high, or because the compound is capable of disproportionation. The first is probable for compounds of the highest valency of a particular element. On the other hand, compounds of the lower valencies may disappear owing to the disproportionation reaction, and if both products of this reaction are formed in the solid state, then the reaction will only proceed readily if it is exothermic. In that case the following reaction is possible:



This process may be broken down into the following stages: the crystal lattice of $MeCl$ must be destroyed (E_1), energy to detach an electron from a single ion of the metal Me^+ must be expended (I_2), energy from the transfer of this electron to another ion of the metal is evolved (I_1), energy of sublimation of the metal formed (s) and lattice energy of the salt $MeCl_2$ formed (E_2) is evolved.





$\Delta\text{H} < 0$, if $|\text{E}_2 + s + \text{I}_1| > |2\text{E}_1 + \text{I}_2|$, and the reaction is then exothermic; $\Delta\text{H} > 0$, if $|\text{E}_2 + s + \text{I}_1| < |2\text{E}_1 + \text{I}_2|$ - the reaction is endothermic.

TABLE 6

Dissociation of halides	Fluorides		Chlorides		Bromides		Iodides		
	ΔH of formation	$\log P_{F_2}$	ΔH of formation	$\log P_{Cl_2}$	ΔH of formation	$\log P_{Br_2}$	ΔH of formation	$\log P_{I_2}$	
$2 MeX_4 = 2 MeX_3 + X_2$	Sc	-	-	-	-	-	-	-	
	Ti	(-380)	-28.4	(-191)	-10.9	(-180)	-13.9	(-141)	-14.0
	V	-325	-18.5	(-162)	-2.6	-129	-5.4	-	-
	Cr	-	-	-110	+11.9	-	-	-	-
	Mn	-230	+10.9	-	-	-	-	-	-
	Fe	-	-	-	-	-	-	-	-
	Co	-	-	-	-	-	-	-	-
	Ni	-	-	-	-	-	-	-	-
	Cu	-	-	-	-	-	-	-	-
	Zn	-	-	-	-	-	-	-	-
$2 MeX_3 = 2 MeX_2 + X_2$	Sc	-367	-	-221	-	-190.4	-	-149	-
	Ti	(-325)	-69.4	(-175)	-24.9	-143	-19.6	-102	-9.6
	V	-285	-48.3	(-160)	-19.0	-120	-3.4	-	-
	Cr	-266	-45.6	-143	-14.5	-102*	-5.1	-99.2	-4.3
	Mn	-238	-22.6	-110	+8.3	-	-	-	-
	Fe	-23.5	-35.0	-96	+0.3	-76	+4.0	-	-
	Co	-	-	-	-	-	-	-	-
	Ni	-	-	-	-	-	-	-	-
	Cu	-	-	-	-	-	-	-	-
	Zn	-	-	-	-	-	-	-	-
$MeX_3 = Me + X_2$	Sc	-	-	-	-	-	-	-	-
	Ti	(-210)	-59.8	-125	-32.7	-110	-27.9	-85	-19.5
	V	-185	-52.1	-117	-29.9	-104	-25.7	-77	-17.2
	Cr	-182	-51.5	-103	-22.9	-81	-18.8	-58	-11.5
	Mn	-190	-54.0	-111.6	-29.0	-96	-23.6	-72	-15.7
	Fe	-168	-46.6	-82	-19.3	-69	-14.7	-45	-7.6
	Co	-158	-43.7	-72	-16.7	-56.4	-11.6	-36	-4.9
	Ni	-158	-43.4	-70.6	-14.6	-55.8	-11.2	-38	-4.6
	Cu	-128	-33.6	-46	-8.5	-34.0	+1.5	-	-
	Zn	-176	-49.1	-99.6	-24.6	-85.7	-20.5	-64.7	-14.1

* The dissociation pressures of fluorides, bromides, and iodides were calculated from [1], and the dissociation pressures of CrBr_3 [17] and of CrI_3 [18] were determined by ourselves.

If it is assumed that the symbatic relationship between the lattice energy and the ionization potential is applicable also to compounds of univalent metals of the first sub-period, then, as Fig. 2 shows, the first ionization potential gradually increases in the transition from Sc to Zn, but the increase is very slow, and I_1 is practically constant from Sc to Cr (Table 7), from Mn to Cu, and is a little greater for Zn. In this case the crystal lattice energy, which should increase even more slowly than the ionization potential, will have an almost constant value. Consequently, the MeCl lattice energy for all these elements, with the exception of zinc, should be either

less than, or equal to, the lattice energy of CuCl. Let us assume that the MeCl lattice energy is equal to the CuCl lattice energy (231 kcal./mole) and let us calculate the change of enthalpy in the disproportionation reaction. The values of ΔH obtained are shown in Table 7.

TABLE 7

Element	I_1	I_2	$\frac{I_2}{I_1}$	$I_2 - I_1$	s (kcal./ / g-atom)	E_2 (kcal./ /mole)	$2E_1 + I_2$	$E_2 + s + I_1$	ΔH (kcal.)
	(kcal./g-atom)		I_1						
Sc	154.1	294.4	1.9	140.3	70	—	—	—	—
Ti	156.6	312.8	2.0	156.2	100	577.4	774.8	-834.0	-59.2
V	155.0	348.0	2.2	193	85	588	810	-828	-18
Cr	154.1	377.4	2.4	223.3	89.4	607	839.4	-850.5	-11.1
Mn	170.4	333.5	1.9	163.1	69.7	568	795.5	-808.1	-12.6
Fe	180.1	365.7	2.0	185.6	96.7	607.5	827.7	-884.3	-56.6
Co	179.4	401.8	2.2	222.4	85	621	863.8	-885.4	-21.6
Ni	174.8	434.2	2.5	259.4	85	647.6	896.2	-907.4	-11.2
Cu	176.4	467.6	2.7	291.2	81.2	649.4	929.6	-907.6	+22.6
Zn	215.5	414.9	1.9	199.4	31.2	643.9	876.9	-890.6	-13.7

As Table 7 and Fig. 10 show, the disproportionation reaction of MeCl proceeds with absorption of energy only in the case of copper. It was assumed that the crystal lattice energy of compounds of the type MeCl is always equal to the lattice energy of cuprous chloride, but as the first ionization potential of Ti, V, Cr, Mn, and Ni is less than that of copper, the lattice energy of their compounds should be a little less than the lattice energy of CuCl, which would make the process still more exothermic. The first ionization potential of Fe, Co, and Ni is greater than that of copper; consequently the MeCl lattice energy for these elements should be somewhat greater, which would make the process less exothermic, but not enough to make it endothermic.

How is this special position of copper in comparison with the other elements to be explained? The disproportionation reaction is exothermic if: $|E_2 + s + I_1| > |2E_1 + I_2|$, that is, when the lattice energy of the dihalide formed, the sublimation energy of the metal, and the first ionization potential exceed the expenditure of energy in the destruction of the monohalide lattice and removal of the second electron from the metal ion.

From Table 7 it is seen that the lattice energy of CuCl_2 is higher than the lattice energies of the other dihalides, but only slightly so. NiCl_2 and ZnCl_2 have almost the same lattice energies as CuCl_2 . The maximum in the case of the second ionization potential, however, is much more prominent. If we take the ratio of the first and second ionization potentials $\left(\frac{I_2}{I_1}\right)$, we see that while for most of the elements this ratio is close to two, copper has a much higher value, nearer to three (2.7). This high value of the second ionization potential is explained by the fact that the second electron lost by the copper is not an s -electron, but a d -electron from the completed $3d^{10}$ -layer. The difficulty of removal of the second electron favors the fact that the expenditure of energy in the disproportionation reaction is not compensated by the evolution of energy in the formation of CuCl_2 and Cu.

Disproportionation of MeCl compounds is also often favored by evolution of a large amount of energy during formation of the metal, that is, by a high sublimation energy. This is not so in the case of copper, the sublimation energy of copper is relatively low. The influence of sublimation energy is more pronounced for the elements of the second and third sub-periods.

SUMMARY

1. It is shown, by a comparison of the dissociation pressures of the elements in the first sub-period, that these pressures change symbatically with the second ionization potential in the transition from one element to another.
2. It is shown that the crystal lattice energies of a number of compounds, both of the elements of the main sub-groups and of the elements of the sub-periods, vary symbatically with changes of the ionization potentials of the metals.
3. It is shown that the dissociation pressures of the tri- and tetrachlorides of the elements of the first sub-period are symbatic with the third or fourth ionization potential respectively of the metal component. On the basis

of this relationship it is possible to predict the possibility or impossibility of synthesizing certain hitherto unknown compounds of a given degree of oxidation of a particular element.

4. On the basis of the symbatic course of the lattice energies and the ionization potentials it is shown why copper forms compounds in which it is univalent. The explanation lies in the high value of the second ionization potential of copper atoms and the relatively low sublimation energy of this metal.

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INTERACTION OF NITRATES AND NITRITES OF THE METALS OF THE FIRST AND SECOND GROUPS OF D. I. MENDELEEV'S PERIODIC SYSTEM IN MELTS

XIII. ELECTRICAL CONDUCTIVITY OF THE BINARY SYSTEMS CESIUM NITRATE - CADMIUM NITRATE, THALLIUM NITRATE - CADMIUM NITRATE, AND POTASSIUM NITRATE - RUBIDIUM NITRATE

P. I. Protsenko and N. P. Popovskaya

Systematic measurements of the electrical conductivities of binary systems in the molten state containing cadmium nitrate as one component and lithium, sodium, potassium, rubidium, cesium, thallium, or silver nitrate as the other, showed that in all these cases the numerical values of the conductivity steadily increase from components of lower to components of higher conductivity: it is noteworthy that the isothermal conductivity curves do not have any distinguishing points which indicate chemical action between the components even when the fusion curves of the diagrams of state for the binary systems, obtained by the visual polythermic method of physico-chemical analysis, clearly show the existence of chemical compounds: $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{RbNO}_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{AgNO}_3$, $\text{LiNO}_3 \cdot \text{RbNO}_3$, $\text{AgNO}_3 \cdot \text{RbNO}_3$, $\text{AgNO}_3 \cdot 2\text{RbNO}_3$ [1-5].

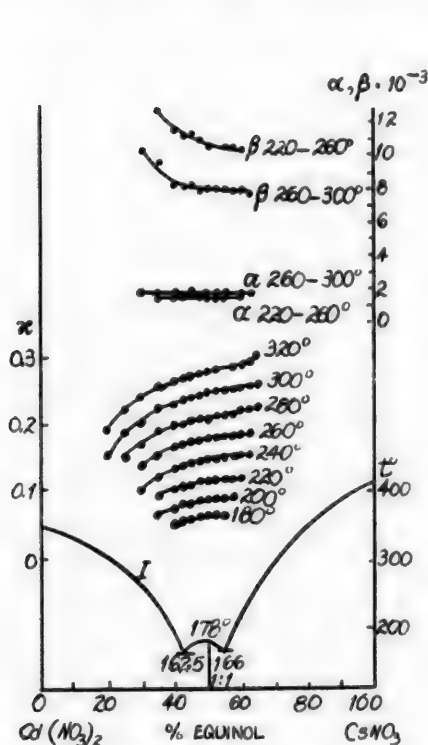


Fig. 1. The system $\text{Cd}(\text{NO}_3)_2$ - CsNO_3 .
 κ) conductivity $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$
are the absolute and relative temperature coefficients.
I) The fusion curve for the system.

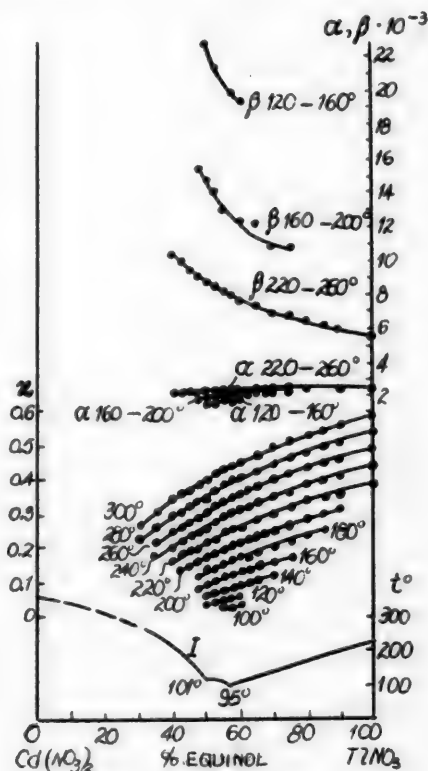


Fig. 2. The system $\text{Cd}(\text{NO}_3)_2$ - TlNO_3 .
 κ) conductivity; $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$ are the absolute and relative temperature coefficients.
I) The fusion curve for the system.

TABLE 1

Cs NO ₃ *	Conductivity, κ						Absolute and relative temperature coefficients					
	160°	180°	200°	220°	240°	260°	280°	300°	320°	220-260°		
										$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
20	-	-	-	-	-	-	-	0.153	0.190	-	-	-
25	-	-	-	-	-	-	0.148	0.1835	0.221	-	-	-
30	-	-	-	-	0.103	0.136	0.1695	0.2045	0.240	-	1.712	10.07
35	-	-	0.064	0.092	0.121	0.153	0.187	0.2235	0.258	1.625	12.50	9.38
40	0.032	0.052	0.0745	0.104	0.1335	0.165	0.1975	0.2300	0.2625	1.525	11.38	8.22
42.5	0.0355	0.0565	0.0795	0.108	0.136	0.1685	0.201	0.234	0.268	1.513	11.00	8.14
45	-	0.060	0.0830	0.110	0.141	0.1725	0.206	0.239	0.271	1.563	11.07	8.09
47.5	-	0.063	0.0860	0.115	0.145	0.1765	0.209	0.242	0.275	1.538	10.69	7.82
50	-	0.064	0.0890	0.117	0.146	0.178	0.210	0.245	0.279	1.525	10.37	7.93
52.5	-	0.065	0.0900	0.118	0.148	0.180	0.212	0.247	0.281	1.550	10.42	7.86
55	-	0.066	0.0895	0.119	0.1485	0.180	0.213	0.249	-	1.5375	10.29	7.94
57.5	-	-	0.0910	0.120	0.150	0.182	0.215	0.250	0.283	1.550	10.29	7.76
60	-	-	-	0.123	0.153	0.186	0.220	0.255	0.288	1.575	10.23	7.82
62.5	-	-	-	-	0.1555	0.189	0.222	0.257	0.2905	-	-	7.63
65	-	-	-	-	-	-	0.226	0.262	0.300	-	-	-

* In equimolar percentages

TABLE 2

TiNO ₃ *	Conductivity, κ											Absolute and relative temperature coefficients					
	100°	120°	140°	160°	180°	200°	220°	240°	260°	280°	300°	120-160°		160-200°		220-260°	
												$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
30	-	-	-	-	-	-	-	-	-	0.220	0.261	-	-	-	-	-	-
35	-	-	-	-	-	-	-	0.171	0.215	0.2595	0.304	-	-	-	-	-	-
40	-	-	-	-	-	-	0.164	0.205	0.249	0.295	0.340	-	-	-	-	2.13	10.30
42.5	-	-	-	-	-	0.136	0.177	0.220	0.264	0.309	0.354	-	-	-	-	2.18	9.90
45	-	-	-	-	-	0.1485	0.190	0.234	0.278	0.323	0.369	-	-	-	-	2.20	9.40
47.5	-	-	-	0.0825	0.1165	0.156	0.199	0.244	0.288	0.334	0.380	-	-	1.825	15.4	2.23	9.20
50	-	0.0345	0.060	0.092	0.130	0.170	0.213	0.257	0.303	0.349	0.396	1.42	22.7	1.95	14.8	2.25	8.70
52.7	-	0.042	0.0715	0.104	0.142	0.184	0.228	0.275	0.322	0.369	0.415	1.55	21.3	2.00	14.0	2.35	8.52
55	0.026	0.049	0.080	0.1185	0.156	0.200	0.247	0.294	0.341	0.387	0.434	1.75	21.2	2.02	12.9	2.35	8.00
57.5	0.0295	0.054	0.086	0.124	0.165	0.210	0.258	0.306	0.353	0.401	0.448	1.75	19.9	2.15	12.9	2.38	7.80
60	0.033	0.059	0.093	0.1325	0.174	0.219	0.266	0.315	0.369	0.410	0.457	1.85	19.5	2.15	12.3	2.38	7.60
62.5	-	-	0.100	0.136	0.177	0.229	-	0.320	0.375	-	-	-	-	-	-	-	-
65	-	-	0.106	0.144	0.188	0.235	0.283	0.330	0.380	0.427	0.474	-	-	2.28	12.28	2.43	7.35
70	-	-	0.122	0.161	0.206	0.254	0.303	0.351	0.400	0.448	0.495	-	-	2.25	10.9	2.43	6.90
75	-	-	-	0.172	0.220	0.268	0.318	0.368	0.417	0.467	0.517	-	-	2.40	10.9	2.48	6.80
80	-	-	-	-	0.239	0.289	0.339	0.389	0.4385	0.488	0.537	-	-	-	-	2.50	6.50
85	-	-	-	-	0.250	0.302	0.352	0.402	0.451	0.501	0.551	-	-	-	-	2.48	6.15
90	-	-	-	-	-	0.317	0.367	0.4165	0.467	0.516	0.566	-	-	-	-	2.50	6.05
100	-	-	-	-	-	-	0.396	0.446	0.498	0.548	0.599	-	-	-	-	2.55	5.72

• In equimolar percentages.

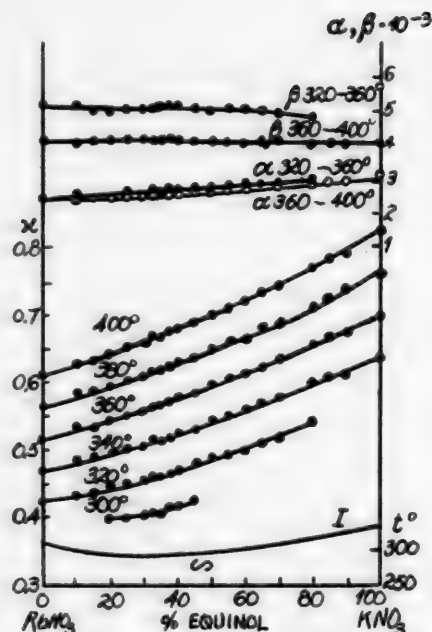


Fig. 3. The system $\text{RbNO}_3\text{--KNO}_3$. κ) conductivity; $\alpha \cdot 10^{-3}$ and $\beta \cdot 10^{-3}$ are the absolute and relative temperature coefficients. I) The fusion curve for the system; (—) continuous solid solutions.

The source of high frequency current was a tube generator which provided a regular supply of sinusoidal electric vibrations. The construction of the generator was such that the frequency range could be varied between 1200 and 2400 cycles per second, with intermediate stages of 1500 and 1900 cycles. The electrical conductivity measurements were carried out at a frequency of 1200 cycles with an output voltage of 6 V.

The platinum electrodes were mounted in a cell of heat-resisting glass, similar in shape to the cell used by Biltz [13] for the measurement of the electrical conductivity of fused salts. The cell was calibrated with the aid of twice-recrystallized chemically pure fused potassium nitrate. The numerical values of the conductivity of potassium nitrate at different temperatures, needed to calculate the cell capacity, were taken from the paper by Jeger and Kapma [14].

The cell constant was systematically checked during the experiments. The electrical conductivity was measured polythermally at $5\text{--}8^\circ$ intervals, in the $100\text{--}400^\circ$ temperature range.

The numerical values of the electrical conductivity, and also of the absolute and relative temperature coefficients, were calculated with the use of a formula, as before [11].

Isotherms, at 20° intervals, were plotted for all the three systems from the data of the polytherms obtained, (Figs. 1, 2, 3). The content of the components in the mixture for the various systems is expressed in equimolar percentages.

DISCUSSION OF RESULTS

As is seen from Figs. 1 and 2 and the data of Tables 1 and 2, the isothermal conductivity curves for the systems $\text{Cd}(\text{NO}_3)_2\text{--CsNO}_3$ and $\text{Cd}(\text{NO}_3)_2\text{--TlNO}_3$ do not have any distinctive points. They all rise steadily from the least conducting cadmium nitrate to the more conducting nitrates of cesium and thallium. It is interesting to note that the isotherms deviate somewhat from additivity in the direction of higher conductivity values.

To confirm the formation of the additionally established compounds $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{CsNO}_3$ and $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{TlNO}_3$ in melts at the moment when the first crystals appear, and to study more deeply the possibility of applying conductivity measurements on melts as a method of physicochemical analysis, although this problem has been solved by a number of workers [6-9], we have examined, in addition to the binary systems described previously [10, 11] three more systems: $\text{Cd}(\text{NO}_3)_2\text{--CsNO}_3$, $\text{Cd}(\text{NO}_3)_2\text{--TlNO}_3$ and $\text{RbNO}_3\text{--KNO}_3$, which are discussed (Figs. 1, 2 and 3).

Study of the binary system $\text{Cd}(\text{NO}_3)_2\text{--CsNO}_3$ showed that chemical action takes place between the nitrates of cadmium and cesium, to form the compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{CsNO}_3$ with melting point 178° (Fig. 1).

In the binary system $\text{Cd}(\text{NO}_3)_2\text{--TlNO}_3$ the nitrates of cadmium and thallium also react chemically and form the complex compound $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{TlNO}_3$ which melts with decomposition (Fig. 2).

In the binary system $\text{RbNO}_3\text{--KNO}_3$ the components form a continuous series of solid solutions with a weakly defined minimum on the fusion curve (Fig. 3).

EXPERIMENTAL

The conductivity measurements were carried out with apparatus set up essentially according to Kohlrausch's scheme, with a number of important modifications and improvements described by Barzakovskiy [12] and by Belyaev and Mironov [8, 9].

The isothermal conductivity curves for the system



also steadily rise from the less conducting rubidium nitrate to the more conducting potassium nitrate. In contrast to the isothermal curves for the first two systems, they show a small deviation from additivity in the direction of lower conductivity values (Fig. 3, Table 3).

TABLE 3

KNO ₃ *	Conductivity, κ						Absolute and relative temperature coefficients			
	300°	320°	340°	360°	380°	400°	320-360°		360-400°	
							$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$	$\alpha \cdot 10^{-3}$	$\beta \cdot 10^{-3}$
0	—	0.422	0.470	0.516	0.563	0.608	2.35	5.19	2.3	4.08
10	—	0.435	0.485	0.535	0.581	0.629	2.5	5.15	2.35	4.03
15	—	0.438	0.486	0.534	0.582	0.630	2.4	4.93	2.4	4.11
20	0.397	0.446	0.494	0.544	0.593	0.642	2.45	4.95	2.45	4.13
25	0.400	0.449	0.500	0.550	0.601	0.650	2.525	5.05	2.5	4.14
30	0.402	0.454	0.504	0.555	0.606	0.656	2.525	5.06	2.525	4.16
32.5	0.406	0.459	0.512	0.564	0.614	0.666	2.625	5.11	2.55	4.12
35	0.408	0.460	0.511	0.564	0.615	0.666	2.6	5.08	2.55	4.125
37.5	0.413	0.464	0.517	0.570	0.622	0.674	2.65	5.125	2.6	4.14
40	0.417	0.470	0.522	0.576	0.628	0.679	2.65	5.08	2.58	4.102
45	0.423	0.476	0.529	0.582	0.635	0.686	2.65	5.00	2.6	4.1
50	—	0.488	0.541	0.596	0.647	0.699	2.7	4.98	2.575	4.01
55	0.438	0.492	0.548	0.602	0.656	0.708	2.75	5.03	2.65	4.02
60	0.444	0.499	0.556	0.610	0.664	0.718	2.775	5.00	2.7	4.05
65	—	0.509	0.566	0.621	0.676	0.732	2.8	4.95	2.78	4.07
70	—	0.519	0.575	0.632	0.687	0.743	2.825	4.91	2.775	4.02
80	—	0.542	0.598	0.656	0.712	0.769	2.85	4.76	2.825	3.95
85	—	—	0.604	0.664	0.722	0.780	—	—	2.9	4.0
90	—	—	0.610	0.670	0.729	0.787	—	—	2.925	4.0
100	—	—	0.635	0.6975	0.7598	0.821	—	—	3.075	4.05

The curves for the absolute temperature coefficient α , calculated from the conductivity data for the temperature ranges 220-260, 260-300° (Fig. 1, Table 1); 120-160, 160-200° (Fig. 2, Table 2); 320-360, 360-400° (Fig. 3, Table 3) are all almost linear. The curves for the relative temperature coefficient β , calculated for the same temperature ranges as the values of the absolute temperature coefficient α , also do not have any distinctive points (Figs. 1-3, Tables 1-3).

The eight systems studied, including those previously described, the components of which interact chemically, do not show any distinctive points on the isothermal conductivity curves which indicate chemical action between the components. Nevertheless it must be stressed again that chemical compounds, clearly shown by the fusion curves, have been established for all these systems by the visual polythermic method of physicochemical analysis.

It follows from the above that there is no correlation in the systems examined between the fusion curves and the isothermal conductivity curves.

Similar cases have been described previously [16, 17]. However, in their generally correct discussions of the problem, the authors concerned relied on insufficient experimental data, and therefore their opinion was not confirmed.

On the other hand, the researches of Bergman and Chagin [6], Luzhanaya and Vereshchetina [15], Tarasova [7], and Belyaev and Mironov [8, 9] showed that when chemical compounds, established by the visual polythermic method of physicochemical analysis, are formed in melts, minima are observed on the isothermal conductivity curves. On the basis of these results, some of the above authors tended to regard as inaccurate the measurements of workers who did not succeed in showing minima on the isothermal conductivity curves corresponding to chemical

* In equimolar percentages.

compounds, while electrical conductivity, as a method of physicochemical analysis, was regarded as a very sensitive method [6-9]. In our opinion, more often there will be no correlation between the fusion and the conductivity curves, for the following reasons.

Fusion curves obtained by the visual polythermic method of physicochemical analysis, reflect the actual nature of the interaction between the components at the solid-liquid interphase at the instant when the first crystals appear, that is, along the liquidus curve. In these conditions the state of the components and the chemical compounds formed is characterized by ideally regular structure of their structural components — crystals, with strict orientation of ions. The isothermal electrical conductivity curves, on the other hand, reflect the state of the components in the fused salt medium, that is, in the liquid phase, and often at temperatures well above the liquidus curve. In these conditions the strictly oriented ionic order characteristic of solid crystals is so changed that the crystals cease to exist as such and pass into an amorphous liquid state, which constitutes, in the present instance, a mixture of "free" positive and negative ions, with a high conductivity.

The abrupt jump from the solid crystalline state into the liquid (fused) state, in our opinion, is accompanied by complete autodissociation* into "free" ions, which happens in the chemical compounds established by us: $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{CsNO}_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{AgNO}_3$, $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{TlNO}_3$, and also in the chemical compounds described by Pushin [1] and Palkin [2], $\text{LiNO}_3 \cdot \text{RbNO}_3$, $\text{AgNO}_3 \cdot 2\text{RbNO}_3$, the electrical conductivity of which was studied by us.

It must be assumed that during the first instant of autodissociation the complex molecules break up into the individual components. The molecules of the components formed (the substances taken originally) in turn undergo autodissociation into "free" ions. The autodissociation of the molecules into free ions of one of the above double salt complexes in melts may be represented by the following scheme:



From the high conductivity of nitrates in melts it may be assumed that their degree of autodissociation will be near to or equal to 100%. In all instances such as those described above, the isothermal electrical conductivity curves will not have any minima to correspond to chemical compounds established by the visual polythermic method of physicochemical analysis.

On the basis of the above considerations it may be assumed that in all analogous cases there will not be any correlation between the fusion curves and the conductivity curves. We may therefore conclude that if the use of electrical conductivity as a method of physicochemical analysis is applicable to melts at all, this is far from always true, and with considerable reservations.

SUMMARY

1. The electrical conductivity of nitrate mixtures in melts of three binary systems: $\text{Cd}(\text{NO}_3)_2$ — CsNO_3 , $\text{Cd}(\text{NO}_3)_2$ — TlNO_3 and KNO_3 — RbNO_3 has been measured and the data used to calculate the absolute and relative temperature coefficients.
2. It is shown that the isothermal conductivity curves steadily rise from the less conducting nitrates of cadmium and rubidium to the more conducting nitrates of thallium, potassium, and cesium, and they do not have any distinctive points, and therefore show no correlation with the liquidus curves obtained by the visual polythermic method of physicochemical analysis.
3. A mechanism is proposed for the autodissociation of double-salt type complexes in melts, formed from nitrates of the first and second groups of Mendeleev's periodic system.
4. It is established that electrical conductivity is not applicable as the basis for a method of physicochemical analysis of melts containing nitrate components, as the conductivity isotherms are always obtained of approximately the same form irrespective of the type of liquidus diagram.

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* The term "autodissociation" is used here in order to stress the difference between the mechanisms of dissociation of molecules into ions in polar solvent media and in melts.

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* T. p. = C. B. Translation pagination.



PHYSICOCHEMICAL STUDY OF AQUEOUS-DIOXANE SOLUTIONS

VII. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN AQUEOUS DIOXANE *

Ya. F. Mezheny

Some physicochemical properties of hydrogen chloride solutions in dioxane were described previously [1]. The present study consisted of an investigation of the electrical conductivity of hydrogen chloride in dioxane-water mixtures with different dielectric constants. The values of the dielectric constants of a number of such mixtures of the same composition as those used by Kraus and Fuoss [2] were taken from that paper. Values for mixtures not given by Kraus and Fuoss were determined graphically. The hydrogen chloride solutions in these solvents were prepared as described previously [1]. The concentrations of the solutions obtained were determined by the usual titration with caustic soda solution in presence of phenolphthalein. Systems with very high dioxane content, and also in anhydrous dioxane, were diluted with water before titration. The solutions of hydrogen chloride in dioxane-water solvent were used in the following dilutions: 10, 100, and 1000 liters/g-equiv. This choice of dilutions made it possible to plot the equivalent conductivity - dilution curves in the region which approached a horizontal line, which was the region of greatest interest in this study. The electrical conductivity of each system was studied at 20, 30, and 40°.

The results of Table 1 show that as the dioxane content of the medium increases and the dielectric constant DC decreases, λ of the HCl solutions decreases, and when the dielectric constant of the medium falls to 8 (10 times as small as DC for water), the equivalent conductivity of the hydrogen chloride solutions is only a few units (that is, its value decreases nearly 100 times). In this medium, the dielectric constant of which is 8, 0.1 N hydrogen chloride solution has lower equivalent conductivity than 0.1 N acetic acid in water. The conductivity of 0.01 N acetic acid in water is, however, about 5 times the conductivity of hydrogen chloride in aqueous dioxane, which has DC equal to 8. If we take hydrogen chloride solutions in anhydrous dioxane, when DC = 2.21, then, as was shown previously [1], the electrical conductivity of such a solution at dilutions of 1000-10 liters/g-equiv. is negligible. Only at dilutions of the order of 0.2 does the equivalent conductivity reach values of the order of tenths of a unit, and the value falls with dilution according to the so-called "anomalous" curve $\lambda = f(v)$. Thus, here also, as for the various solvents studied by Kablukov, the electrical conductivity of hydrogen chloride solutions entirely depends on the dielectric constant of the aqueous dioxane medium. It is also interesting to note that similar values for the electrical conductivities of hydrogen chloride solutions are obtained irrespective of whether the solvent is pure or a mixture. Kablukov found, for solutions in methyl alcohol, the dielectric constant of which is 35.4, an equivalent conductivity of 117 at a dilution of 91.16; for a dioxane-water mixture (DC = 37) at the same dilution we have an equivalent conductivity of about 123.

The variation of the electrical conductivity of HCl solutions in dioxane-water mixtures on temperature (in the temperature range studied) is approximately represented by a linear function with different slopes to the temperature axis: it is greatest for systems with DC = 37; in systems with DC = 12, the temperature coefficient remains positive but has a lower absolute value.

λ_0 of hydrogen chloride solutions

As Table 1 shows, the $\lambda = f(v)$ curves for dioxane-water solutions of hydrogen chloride lie lower with decreasing DC of the medium (Fig. 1).

As is known, by transformation of the function $\lambda = f(v)$ into the function $\lambda = f(\sqrt{c})$ values of λ_0 may be obtained by extrapolation, that is, values of equivalent conductivity corresponding to $a = 1$ (the classical theory).

* Presented at the extended meeting of the Learned Council of the Institute of General and Inorganic Chemistry, Academy of Sciences, Ukrainian SSR, April 1, 1952.

But, as Fig. 2 shows, the $\lambda = f(\sqrt{C})$ curves also lie lower with decreasing DC of the medium, and so the values of λ_0 decrease also, and when $DC \rightarrow 1$, $\lambda_0 \rightarrow 0$.

TABLE 1

Electrical Conductivity of Hydrogen Chloride in Aqueous Dioxane Media

Percentage of water in the dioxane mixture	DC	Dilution, liters/g-equiv.	Temperature	$\chi \cdot 10^3$	λ
82	60	10	20°	16.3	163
	60	100	20	2.02	202
	60	1000	20	0.215	215
53	37	10	20	8.76	87.6
	37	10	30	8.95	89.5
		10	40	12.0	120.0
	37	100	20	1.275	127.5
		100	30	1.523	152.3
		100	40	1.752	175.2
	37	1000	20	0.132	132.0
		1000	30	0.163	163.2
		1000	40	0.204	204.0
20.2	12	10	20	0.867	8.67
		10	30	1.05	10.5
	12	100	20	0.0936	9.36
		100	30	0.1027	10.27
		100	40	0.1062	10.62
	12	1000	20	0.011	11.0
		1000	30	0.021	21
		1000	40	0.025	25
14	8	10	20	0.261	2.61
		10	25	0.288	2.88
		10	30	0.303	3.03
		10	40	0.316	3.16
	8	100	20	0.0376	3.76
		100	25	0.0432	4.32
		100	30	0.0473	4.73
		100	40	0.0521	5.21
	8	1000	18	0.00405	4.05
		1000	20	0.00427	4.27
		1000	25	0.00452	4.52

It is known from the work of Owen and Waters [4], who measured the electrical conductivity of hydrogen chloride solutions in dioxane-water mixtures at $DC = 60, 79, 38, 48, 27$ and 9.53 at 25° (these results are also quoted in the book by Harned and Owen [5], p. 326) • that the equivalent conductivity curves plotted against the square root of the concentration also form a group of curves which lie lower with decreasing DC of the medium. This tendency of $\lambda_0 \rightarrow 0$ as DC of the medium tends to unity, follows both from Kablukov's data [3] and from the data of other workers (Table 2).

These results can be explained only if we admit the possibility of the process $H^+ + Cl^- \rightarrow HCl$ which goes increasingly toward the right as the dielectric constant of the medium decreases, even in very dilute solutions.

• Although Chapter 11 of this book is exclusively devoted to the properties of HCl solutions, it makes no mention whatever of the classic investigations by the Russian scientist I. A. Kablukov, who was the first to study the electrical conductivity of non-aqueous solutions of hydrogen chloride.

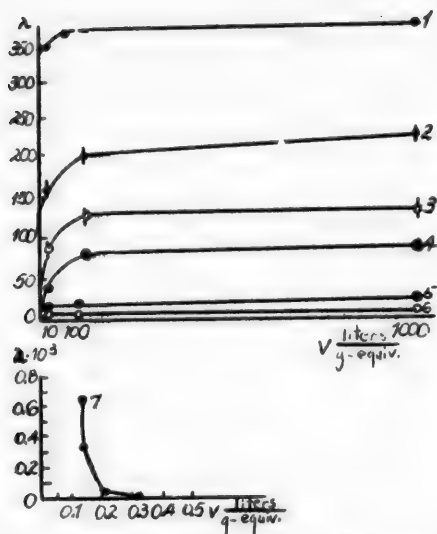


Fig. 1. Variation of the equivalent conductivity of HCl solutions in dioxane-water medium at 20°.

1) In water (DC = 80), 2) in dioxane-water medium (DC = 60), 3) in dioxane-water medium (DC = 37), 4) the same for DC = 20, 5, 6) the same, with increase of dioxane content and decrease of DC to 12 and 8 respectively, 7) the same for pure dioxane, with DC = 2.1.

$\lambda = f \frac{1}{D}$ curve for solutions of HCl in any medium (Fig. 3).

If the data obtained in the present study are used to plot the graph for the function

$$\log \frac{\lambda_u}{\lambda_p} = f \frac{1}{D} \quad (1)$$

then this will be a straight line which does not pass through the origin; therefore, for hydrogen chloride solutions, the equation for the relationship between λ and D may be given in the form

$$\lambda_p = \lambda_u \cdot 10^{-(20.5 \cdot \frac{1}{D} + 0.5)} \quad (2)$$

or

$$\lambda_p = 1500 \cdot 10^{-(20.5 \cdot \frac{1}{D} + 0.5)}$$

Quite obviously this equation loses its meaning when $\frac{1}{D} \approx 0$, since when $D \rightarrow \infty$ and $\frac{1}{D} \rightarrow 0$, not only ionic triads but simple undissociated molecules are absent, as is the mobility-decreasing action of the charge of one ion on another; therefore in such conditions the equations (2) become

$$\log \frac{\lambda_u}{\lambda_p} = k \cdot \frac{1}{D} \quad (3)$$

or

$$\lambda_p = \lambda_u \cdot e^{-k \cdot \frac{1}{D}} \quad (4)$$

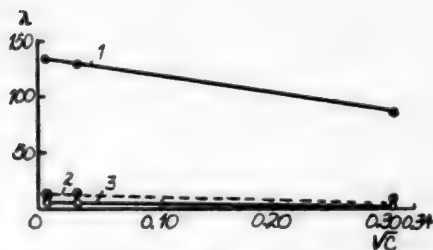


Fig. 2. $\lambda = f(\sqrt{C})$ for dioxane-water solutions of hydrogen chloride.

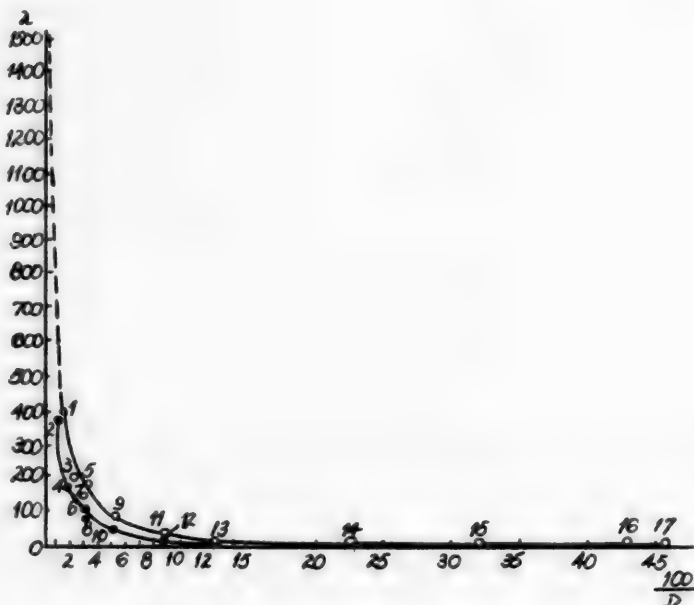
1) At DC = 37, 2) at DC = 12, 3) at DC = 8.

The values for λ_0 determined by ourselves from Fig. 2 for media with low dielectric constants, like the values obtained by Owen and Harned [5], are meaningless, as these values for the equivalent conductivity do not correspond to that state of the electrolyte ($\alpha = 1$) which is necessary for λ_0 and which the theory of strong electrolytes demands for all media. Semenchenko [6] was right in pointing out "that in solvents with low dielectric constants molecularization of ions, and even formation of complex ions and molecules is possible, which is completely ignored by the Debye-Onsager theory" (*italics ours*). This is also indicated by the

TABLE 2

Decrease of the Values of λ_0 of HCl Solutions with Decrease of DC of the Medium

Medium		t°	λ_0	Sources
Substance	DC			
Water	80	25	≈ 425	[11]
Methyl alcohol	33	25	133.1	[6]
Dioxane + water	37	18	137	Our data
Ethyl alcohol	25	25	62 (66.5)	[7]
Propyl alcohol	20.1	25	46.6	[9]
Butyl alcohol	17.8	25	20	[9]
Dioxane + water	8	20	≈ 5	Our data
Benzene	2.2	18	≈ 0	[3]
Dioxane	2.1	18	≈ 0	Our data

Fig. 3. $\lambda = f\left(\frac{1}{D}\right)$ for hydrogen chloride solutions.

1) Aqueous solution, $v = 1000$ liters/g-equiv., 2) aqueous solution, $v = 10$ liters/g-equiv., 3) dioxane-water solution for $DC = 60$ and $v = 1000$ liters/g-equiv., 4) dioxane-water solutions for $DC = 60$ and $v = 10$ liters/g-equiv., 5) in methyl alcohol for $DC = 33$ and $v = 1000$ liters/g-equiv. [9], 6) in methyl alcohol for $DC = 33$ and $v = 10$ liters/g-equiv., 7) dioxane-water solution for $DC = 37$ and $v = 1000$ l/g-equiv., 8) dioxane-water solution for $DC = 37$ and $v = 10$ liters/g-equiv., 9) dioxane-water solution for $DC = 20$ and $v = 1000$ liters/g-equiv., 10) dioxane-water solution for $DC = 20$ and $v = 10$ liters/g-equiv., 11, 12) dioxane-water solutions for $DC = 12$ and $v = 1000$ and 10 liters/g-equiv., 13) dioxane-water solution for $DC = 8$ and $v = 1000$ liters/g-equiv., 14) in ethyl ether for $DC = 4.5$ [3], 15) dioxane-water solution for $DC = 2.12$ [10], 16) in benzene for $DC = 2.28$ [3], 17) in dioxane for $DC = 2.1$.

The results of a check of the agreement between data calculated from Equations 1-3 and experimental data obtained both by ourselves and by other workers in various media are shown in Table 3.

TABLE 3

Comparison of Theoretically Calculated and Experimentally Determined Values of the Equivalent Conductivity of Hydrogen Chloride

Substance	Medium	$\lambda_{\text{calc.}}$	$\lambda_{\text{exp.}}$	Source	Relative deviation (%)
	DC				
Water	80	264	370	Tech. Encyclopedia	40
Dioxane + water	37	137	132	Our data	-3
	20	44	58		30
	12	9.8	11		12
	8	4.52	4.05		-10
Methyl alcohol	33	113	133	[12]	17
Ethyl alcohol	25	72	74		2
Propyl alcohol	20.1	44.2	37.26	[13]	-20
Butyl alcohol	17.8	33	18.53		-44
Ethyl ether	4.45	$1.7 \cdot 10^{-2}$	$0.58 \cdot 10^{-2}$	[8]	-60
Dioxane	2.1	$10^{-6.5}$	Very small for $v = 1000$	Our data	Same order of magnitude

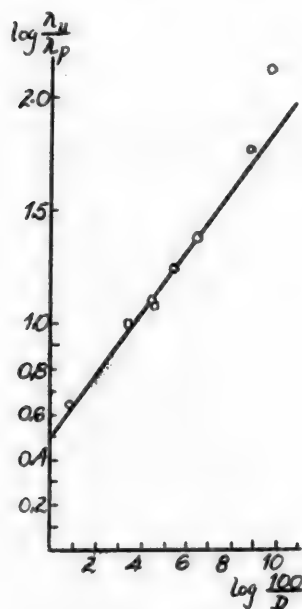


Fig. 4. Variation of $\log \frac{\lambda_u}{\lambda_p}$ with $\frac{1}{D}$ for hydrogen chloride solutions.

from the experimental results, and therefore the agreement of our experimental data with those calculated with the aid of equations (1, 2) should be regarded as satisfactory.

SUMMARY

1. The specific and equivalent conductivities of hydrogen chloride in aqueous dioxane solutions at DC between 80 and 2.1 have been measured.
2. It is shown that the equivalent conductivity of hydrogen chloride solutions decreases regularly with decreasing DC of the medium. The explanation for this is that when $DC \rightarrow 1$, $\alpha \rightarrow 0$ and $\lambda_0 \rightarrow 0$.

The data of Table 3 shows that the order of magnitude of the equivalent conductivity of hydrogen chloride solutions may be predicted with the aid of the mathematical relationships (1, 3).

In 11 instances when the theoretically calculated and experimentally found values of the electrical conductivity were compared, 2 showed a relative deviation from 3 to 2%; 4 gave relative deviations from -20 to 30%, 2 gave relative deviations from -40 to 40%, and only one gave a relative deviation of -60%; here, as was already pointed out for media with larger values of DC (80), the term B in equation (3) should increasingly lose its meaning, and therefore it is better to use equation (4) for such media.

The agreement, shown in Table 3, between the calculated and the experimental values of electrical conductivity confirms the validity of the view that the ions of a strong electrolyte form molecules when it is transferred to media with decreasing values of the dielectric constant, even in greatly diluted solutions.

As is known [6], the Kohlrausch-Onsager equation, even with such a conveniently investigated electrolyte as an aqueous solution of potassium chloride (which is non-volatile, non-hygroscopic, stable to oxidation and reduction, etc.), gives results which deviate by 32.2 to 21.4%

3. The agreement between the values of the equivalent conductivity calculated with the aid of the proposed equation and the experimental values has been checked. Satisfactory agreement was found.

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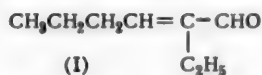
* In J. Gen. Chem., 1954 the only other article by this author in addition to the one just concluded, appears on page 1945, T.p. 1911. (T.p. = C. B. Translation pagination) — Publisher

STUDY OF THE CATALYTIC CONVERSION OF ALCOHOL INTO HYDROCARBONS OF THE DIVINYL SERIES

XVIII. CONTACT CONVERSION OF BUTYRALDEHYDE INTO 2-ETHYLHEXEN-2-AL

Yu. A. Gorin, K. N. Charskaya, and V. P. Litvinovskaya

In the presence of certain alkaline and also acid agents butyraldehyde undergoes aldol condensation with the formation of butyraldol [1]. The latter, being an unstable compound, readily gives up water when heated or treated with dehydrating agents and is converted into 2-ethylhexen-2-al (I).



Raupenstrauch [2] prepared 2-ethylhexenal by heating butyraldehyde with sodium acetate solution or 10% caustic soda solution. Gorhan [3] prepared 2-ethylhexenal from butyraldehyde by heating it with dilute sulfuric acid or fuming hydrochloric acid. Weizmann and Garrard [4] also prepared 2-ethylhexenal by the action of caustic potash solution on butyraldehyde. Batalin and Slavina [5] prepared butyraldol by heating butyraldehyde with 10% caustic potash solution. The butyraldol was converted into 2-ethylhexenal by heating it with sulfuric acid. These same workers also studied the properties of 2-ethylhexenal in greater detail.

Gorin [6], who studied the mechanism of the contact synthesis of divinyl from ethyl alcohol by S. V. Lebedev's method [7], concluded that an intermediate stage in this complex reaction is the condensation of acetaldehyde accompanied by removal of water and formation of crotonaldehyde, which is later reduced to crotyl alcohol, which is then dehydrated to divinyl.

Gorin and Vasileva [8] studied the conversion of n-butyl alcohol with the aid of Lebedev's catalyst. It was shown that in these conditions butyl alcohol forms diethylenic hydrocarbons C_8H_{14} , the carbon skeleton of which corresponds to the skeleton of 3-methylheptane which is formed by their hydrogenation. These hydrocarbons form an isomeric mixture: 3-methylheptadiene-3,5, 3-methylheptadiene-2,4, and 2-ethylhexadiene-1,3. These authors presumed that, by analogy with the conversion of ethyl alcohol to divinyl, the intermediate stages of the reaction should be effected through butyraldehyde, formed by dehydrogenation of butyl alcohol, condensation of butyraldehyde to 2-ethylhexen-2-al, its reduction to 2-ethylhexen-2-ol-1, and dehydration of the latter to diethylenic C_8H_{14} hydrocarbons.

Thus, the contact synthesis of diethylenic hydrocarbons from primary alcohols by this scheme passes through the intermediate stage of condensation of aldehydes formed by the dehydrogenation of alcohols by the dehydrogenating component of the catalyst.

In order to verify the above scheme for the contact synthesis of diethylenic hydrocarbons from n-butyl alcohol, we carried out experiments on the conversion of butyraldehyde by Lebedev's catalyst and by its dehydrogenating and dehydrating components.

The results showed that both components of the catalyst cause condensation of butyraldehyde and its conversion into 2-ethylhexen-2-al, and under equal experimental conditions the yield of the latter is greater on the dehydrogenating than on the dehydrating component of the catalyst. Butyraldehyde condensation also takes place on a catalyst consisting of a mixture of the components. Thus, the action of Lebedev's catalyst or of its separate components on butyraldehyde is analogous to the action of alkaline or acid reagents, which results in the condensation of butyraldehyde to butyraldol and an unsaturated aldehyde (2-ethylhexenal). The 2-ethylhexenal isolated from the catalytic conversion products of butyraldehyde was confirmed by its boiling point, density, formation of

TABLE 1

Experiments on the Contact Conversion of Butyraldehyde on Lebedev's Catalyst and on its Components

Expt. No.	Catalyst	Temperature	Amount			Fractionation of upper condensate layer.					Amount				Yield of 2-ethylhexen-2-al as % of the butyraldehyde		
			Of gas obtained (in liters at 0° and 760 mm) (without air)	Of condensate obtained (in g)	Of water in condensate (%)	Amounts of fractions (%)					Of 2-ethylhexen-2-al in 150-200° fraction				Of reacted butyraldehyde (g)	Per pass	
						Up to 100°	100-150°	150-200°	Residue	Losses	In g	In %	In g	In %			
1	Component A	400°	7.9	57.3	14.8	23.8	21.4	12.3	40.2	2.3	2.3	41.5	3.4	32.0	74.0	3.0	3.1
2	"	400	9.3	46.8	42.9	12.4	21.0	17.3	30.6	11.7	0.3	6.2	1.0	19.5	76.4	0.39	0.4
3	"	350	2.9	69.5	9.3	32.4	12.0	26.6	26.3	2.7	10.0	59.7	14.1	68.9	63.3	12.9	15.8
4	"	350	3.5	60.7	28.8	32.8	12.2	15.3	30.8	8.9	2.7	40.6	8.0	56.0	69.4	3.5	3.9
5	"	300	2.0	71.8	9.8	26.5	11.7	31.2	26.4	4.2	12.8	63.3	12.5	73.1	64.9	16.5	19.8
6	"	300	1.4	70.5	12.5	48.7	4.5	18.6	24.0	4.2	5.6	49.2	16.2	53.9	61.2	7.2	9.1
7	"	250	0.5	72.2	7.2	35.1	8.2	31.3	24.6	0.8	13.2	63.2	19.0	80.9	58.4	17.1	22.7
8	"	350	0.3	72.8	4.3	57.7	1.6	24.7	14.9	1.5	9.1	54.1	27.6	68.5	49.8	11.8	15.6
9	Catalyst	375	8.2	61.9	20.4	15.4	43.2	10.5	26.5	4.4	1.4	28.5	1.5	19.6	75.9	1.8	1.9
10	"	300	5.9	67.5	17.8	22.4	31.0	15.1	27.7	3.8	4.1	49.1	7.2	57.6	70.2	5.3	5.8

NOTE. A is the dehydrogenating and B is the dehydrating component of the catalyst.

a semicarbazone with a characteristic melting point, addition of the theoretical amount of hydrogen on hydrogenation, and determination of the carbonyl group content, which agreed with the calculated value for 2-ethylhexanal, with the aid of hydroxylamine.

The formation of 2-ethylhexen-2-al, which has a branched carbon skeleton, from butyraldehyde explains, in accordance with the scheme outlined above, the formation from n-butyl alcohol of C_8H_{14} hydrocarbons with the same carbon skeleton as 2-ethylhexenal.

EXPERIMENTAL

The reaction of contact condensation of butyraldehyde to 2-ethylhexen-2-al was studied on both components of Lebedev's catalyst and on Lebedev's catalyst itself, at several temperatures.

The butyraldehyde used was prepared by catalytic dehydrogenation of butyl alcohol. After being dried, the butyraldehyde was distilled.

B. p. 73.5°; d_4^{20} 0.8074; the content of C_4H_7CHO in the product, determined with the aid of hydroxylamine hydrochloride, was 95.6%.

The contact conversion of butyraldehyde was carried out in a quartz tube 70 cm long, 30 mm diameter, surrounded by an electric heating element. The tube was charged with 200 ml of the catalyst prepared in the form of turnings. The catalyst was activated at 500° for 2 hours before the experiments. One experiment was carried out on each portion of catalyst. In each experiment 100 ml (77.4 g) butyraldehyde was passed through a furnace. The temperature was measured with a thermocouple, the hot junction of which was inserted in the center of the catalyst layer. The liquid and gaseous reaction products were collected in the usual manner. The composition of the gaseous products of each experiment was determined with the aid of the Orsat apparatus.

All the condensates obtained in the experiments were in two layers. The upper oily layer was separated from the lower aqueous layer, dried over calcium chloride, and distilled from a round-bottomed flask with a double bulb dephlegmator; fractions of up to 100°, 100-150°, and 150-200° were taken. The amount of unreacted butyraldehyde was determined in the fraction boiling below 100° with the aid of hydroxylamine hydrochloride. The amount of aldehydes found by the same method in the 150-200° fraction was taken as 2-ethylhexen-2-al. The presence of the latter, as will be seen below, was confirmed in this fraction.

The results of the experiments are shown in Tables 1 and 2.

TABLE 2

Gas Composition in Experiments on the Contact Conversion of Butyraldehyde (in Volume %)

Expt. No.	Catalyst	Temperature	Substances absorbed by alkali	$C_3H_6 + C_4H_8$	C_2H_4	CO	H_2	C_nH_{2n+2}
1	Component A	400°	15.0	14.3	6.2	0.7	58.4	5.4
2	" B	400	1.7	52.4	4.3	0.3	27.6	13.7
3	" A	350	17.1	3.8	2.6	0.0	76.5	0.0
4	" B	350	5.1	38.9	1.4	1.2	53.4	0.0
5	" A	300	18.4	6.5	2.4	0.0	72.7	0.0
6	" B	300	16.5	20.5	3.5	0.0	59.5	0.0
7	" A	250	54.9	1.8	0.0	0.9	42.4	0.0
8	" B	250	22.8	24.1	6.7	0.0	46.4	0.0
9	Catalyst	375	30.4	12.8	2.6	6.3	53.9	0.0
10	"	300	34.1	9.5	2.1	0.3	54.0	0.0

It is seen from the results in Table 1 that the yield of 2-ethylhexen-2-al increased with decreasing temperature. The yield of 2-ethylhexen-2-al was higher on the dehydrogenating than on the dehydrating component of the catalyst.

The gaseous reaction products (Table 2) contained hydrogen formed as the result of dehydrogenation of butyraldehyde condensation products. In addition, unsaturated C_2 , C_3 , C_4 hydrocarbons were found, formed by the decomposition of butyraldehyde and its condensation products by the action of the high temperature and the

catalyst. As was to be expected, the ratio hydrogen/unsaturated hydrocarbons was higher in the gas from experiments on the dehydrogenating than the dehydrating component. The nature of the substances absorbed by alkali, the amounts of which increased with decrease of the experimental temperature, was not established. The amount of carbon dioxide in the gas was insignificant, as was proved by means of baryta water.

Determination of 2-ethylhexen-2-al. in the products of the contact conversion of butyraldehyde

To accumulate the reaction products, 3 experiments were carried out on the dehydrogenating component of the catalyst at 300°. In each experiment 200 ml butyraldehyde was passed through the furnace. After each experiment the catalyst was regenerated in a current of air at 500°. The condensates obtained in each experiment were separated from the aqueous layer, combined, dried over calcium chloride and distilled from a round-bottom flask with a four-bulb dephlegmator.

The amount distilled was 401 g, and the following fractions were obtained: 1st, b.p. up to 80°, 46.5%; 2nd, b.p. 80-160°, 14.6%; 3rd, b.p. 160-173°, 15.7%; residue 20.6%; loss 2.6%.

By repeated fractionation of the 160-173° fraction, a narrow fraction was isolated which boiled in the range 172-173°, which corresponded to 2-ethylhexen-2-al. [5]; d_4^{20} 0.8549.

Hydrogenation, by Ginzberg's [9] method: 0.3066 g substance added on 54.5 ml H_2 (NTP). Hydrogen number (per one ethylene bond; addition of hydrogen to the aldehyde group may be neglected, as its rate is negligibly low [10]): found 177.75. $C_7H_{13}CHO$. Calculated 177.78. Carboxyl group content (as %, determined by hydroxylamine): found 20.60, 20.73. $C_7H_{13}CHO$. Calculated: 22%.

The semicarbazone consisted of white crystals which melted at 150-151° after recrystallization from methyl alcohol. The fraction with b.p. 172-173°, isolated from the products obtained in the experiments on the contact conversion of butyraldehyde on the dehydrating component of the catalyst, gave a semicarbazone with the same melting point.

Literature data for 2-hexen-2-al: d_4^{20} 0.8528 [4]; semicarbazone, m.p. 150-151° [5].

Thus, the presence of 2-ethylhexen-2-al in the products of the contact conversion of butyraldehyde on the components of Lebedev's catalyst can be considered as established.

SUMMARY

1. The catalytic conversion of butyraldehyde on the dehydrogenating and dehydrating components of Lebedev's catalyst at 250, 300, 350, and 400°, and on the catalyst itself at 300 and 375° was studied.
2. It is shown that in these conditions condensation of butyraldehyde with formation of 2-ethylhexen-2-al takes place. The yield of 2-ethylhexen-2-al decreases with increasing temperature, in the temperature range studied.
3. It is shown that, at equal temperatures, the yield of 2-ethylhexen-2-al is higher on the dehydrogenating than on the dehydrating component of the catalyst.

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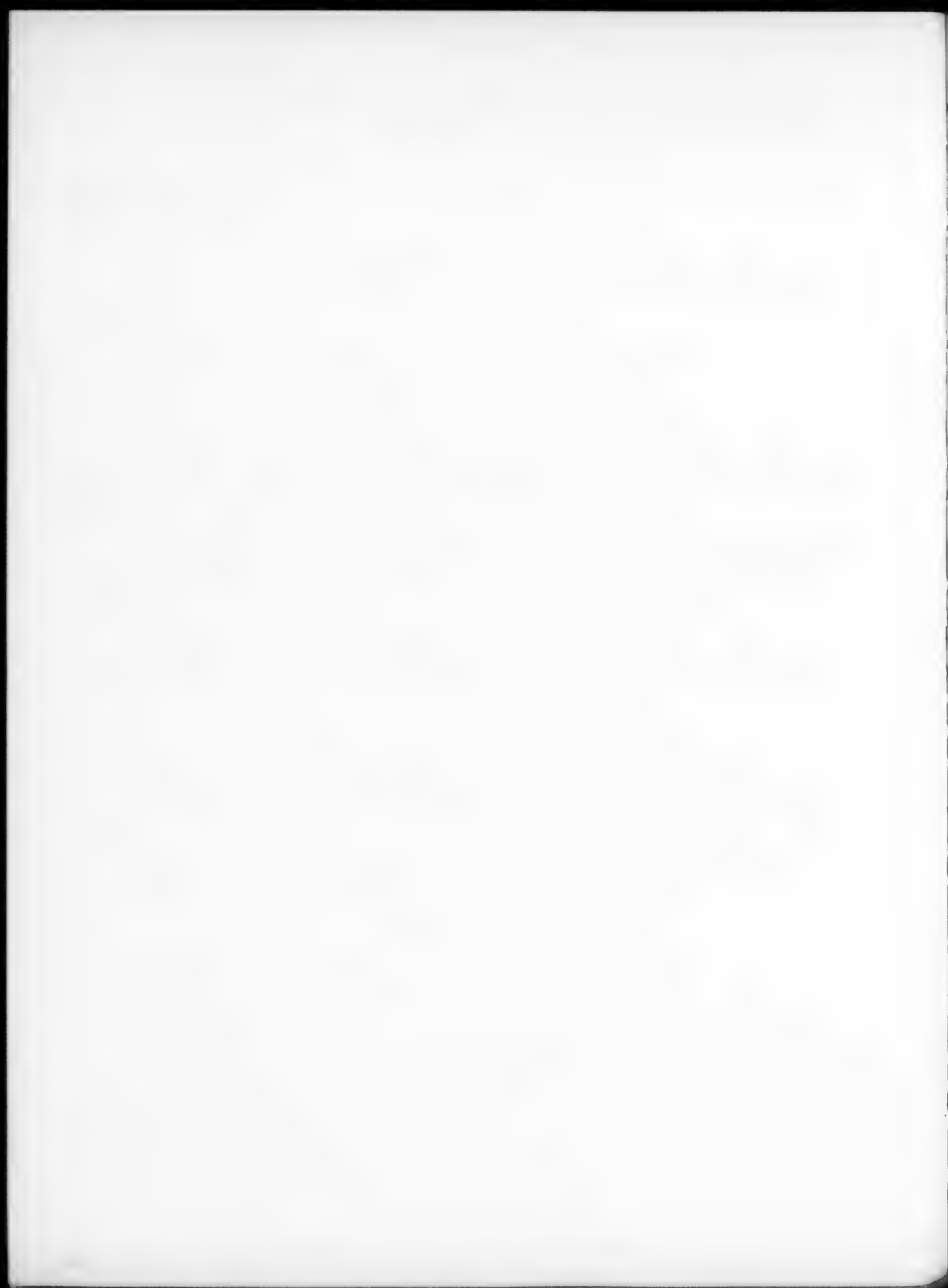
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INVESTIGATIONS OF CONJUGATED SYSTEMS

LVI. CONDENSATION OF DIENE HYDROCARBONS WITH PROPARGYL ALDEHYDE

A. A. Petrov

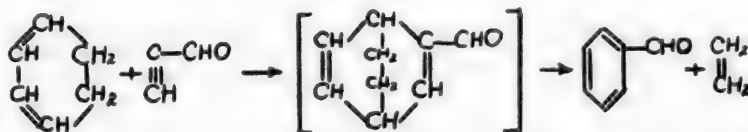
In a series of previous articles, diene syntheses with the aid of butynone were described by the present author [1-6]. Simultaneously with our first papers on the subject, communications by other authors on the condensation of various acetylenic ketones with diene hydrocarbons were published [7, 8]. Nevertheless, the homocyclization of dienes with acetylenic aldehydes of the aliphatic series remained almost unstudied. There is only one paper, which deals with the reactions of tetrolic aldehyde and heptyne aldehyde with divinyl and trimethylbutadiene [9], and patent data [10] which largely do not correspond to reality; therefore, having the opportunity of working with propargyl aldehyde, the author has set himself the task of filling this gap to some extent.

In the present paper the reactions of propargyl aldehyde with divinyl, diisopropenyl, cyclopentadiene, and cyclohexadiene are described. When this aldehyde was heated for a short time with divinyl and diisopropenyl at 115°, $\Delta^{1,4}$ -dihydrobenzoic and 4,5-dimethyl- $\Delta^{1,4}$ -dihydrobenzoic aldehydes were obtained. The first of these substances is a colorless liquid and the second consists of crystals similar in odor to benzaldehyde.

It was shown by the use of dihydrobenzaldehyde as an example that these substances do not have a conjugated system of carbon-carbon double bonds, as their physical constants are unchanged when they are heated with maleic anhydride. They are readily dehydrogenated on heating with sulfur to form the corresponding aromatic aldehydes. The rings are oxidized and ruptured by permanganate treatment. Oxidation by silver oxide gives acids of more complex structure. The substances react easily with hydrazine derivatives.

Cyclopentadiene reacts with propargyl aldehyde even at ordinary temperatures, with great evolution of heat. The reaction is accompanied by polymer formation. Endomethylenedihydrobenzaldehyde is a liquid with a pungent smell. It resinifies on keeping.

When cyclohexadiene is heated with propargyl aldehyde, benzaldehyde and ethylene are formed. Benzaldehyde was identified by its physical constants and by the melting point of its p-nitrophenyl hydrazone. The ethylene was converted into dibromoethane. Similar removal of the endoethylene bridge was observed in the condensation of cyclohexadiene with butynone [6].



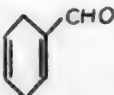
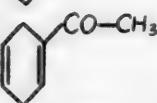
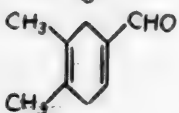
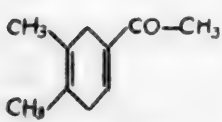
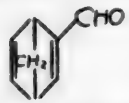
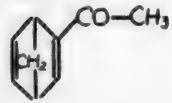
The constants of the hydroaromatic aldehydes obtained are compared in Table 1 with the constants of the analogously constituted cyclohexadiene ketones described in the previous communication.

It is seen from Table 1 that the aldehydes have somewhat higher values for the exaltation of molecular refraction than do the ketones. Their boiling points differ by 12-15°.

A French patent [10] gives only the boiling points, 77-78 and 82-84° (12 mm), for the condensation products of propargyl aldehyde with diisopropenyl and trimethylbutadiene, while for the condensation product of tetrolic aldehyde with isoprene, the boiling point, 90-95° (12 mm), d^{20}_4 0.962 and n^{20}_D 1.4693 are given. It is obvious that the author of these patents did not have these aldehydes at his disposal, as the constants given differ greatly from those determined by us and given in the above-mentioned English paper (for the substances named in the patent and others of analogous structure) [9].

It was shown in earlier papers (jointly with Sopov [4, 5]) that cyclohexadiene ketones react with organo-magnesium compounds to form the corresponding tertiary alcohols which give, on dehydration, hydrocarbons either of the vinylhexadiene or of the aromatic class, according to conditions. The relative yields of the two depend on the structure of the original alcohol and the nature of the catalyst.

TABLE 1

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR _D		Melting point		
				Found	Calculated	Semi-carbazone	p-nitro-phenyl-hydrazone	2-4-dinitro-phenyl-hydrazone
	80°	1.0230	1.5182	32.04	31.40	204-205	197-198	226°
	94 [1,2]	1.0168	1.5150	36.12	36.02	200	204	—
	112-113, m.p. 32.5-33.5	—	1.5176	—	—	230	218-219	233-234
	127.5- 128 [1,2]	0.9868	1.5118	45.26	45.63	225-226	214-215	234-235
	80	1.0574	1.5218	34.64	33.82	—	—	—
	92 [1,2]	1.0362	1.5098	38.71	38.44	—	—	—

In the light of these results considerable interest is attached to the study of the dehydration of secondary alcohols of analogous structure, which could be easily obtained from the hydroaromatic aldehydes described above.

The corresponding secondary alcohols were obtained by the action of methylmagnesium iodide and ethylmagnesium bromide on dihydrobenzaldehyde, without any appreciable admixture of cyclohexene ketones, which are possible by-products in this reaction.

The secondary alcohol from endomethylenedihydrobenzaldehyde was obtained in an analogous manner. We must point out here that we did not succeed previously in obtaining a tertiary alcohol from methyl(endomethylene)-cyclohexenyl ketone, as a more saturated ketone was obtained [6].





The action of methylmagnesium iodide on dimethyldihydrobenzaldehyde gave a secondary alcohol with an admixture of a carbonyl-containing compound.

In contrast to tertiary alcohols of this series, the secondary alcohols are easily isolated from the reaction mixture and can be distilled in a vacuum without apparent decomposition. These substances are colorless and almost odorless liquids. As Table 2 shows, their molecular refraction values are rather below the calculated values. This was also found for the tertiary alcohols of analogous structure.

The secondary alcohols were dehydrated by distillation over solid alkali, distillation with a small amount of iodine or p-toluene sulfonic acid, distillation with 10% oxalic acid solution, or by the action of acetic anhydride

and a drop of H_2SO_4 in the cold. In all cases mainly aromatic hydrocarbons were formed, with small amounts of unsaturated hydrocarbons. Change of the nature of the catalyst had practically no effect on the properties of the reaction product.

TABLE 2

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	M_R^D	
				Found	Calculated
 CH(OH)-CH_3	103.5°	0.9943	1.5068	37.15	37.53
 $\text{C(OH)(CH}_3)_2$	97.5	0.9783	1.5012	41.61	42.15
 $\text{CH(OH)-C}_2\text{H}_5$	111-112	0.9778	1.5022	41.73	42.15
 CH(OH)-CH_3	94-96	1.0140	1.5008	39.56	39.95

In this way methylcyclohexadienyl carbinol was converted into ethylbenzene, ethylcyclohexadienyl carbinol into propylbenzene, and methyltrimethylcyclohexadienyl carbinol into 1,2-dimethyl-4-ethylbenzene.

It must be pointed out that secondary cyclohexenic alcohols do not split off water in the conditions described above.

Thus, it was established as a result of this study that secondary cyclohexadiene alcohols split off water as easily as the tertiary; however, in the former instance dehydration is accompanied by a greater degree of isomerization, and vinylcyclohexadiene hydrocarbons cannot be isolated as intermediate products.

EXPERIMENTAL

Propargyl aldehyde was obtained by oxidation of propargyl alcohol with sodium dichromate with continuous distillation of the reaction products in a vacuum [11]. The divinyl used was technical grade (99.8%). Di-isopropenyl was prepared by dehydration of pinacol with the aid of acetic anhydride and a few drops of orthophosphoric acid, cyclopentadiene — by depolymerization of technical dicyclopentadiene, cyclohexadiene — by distillation of 1,2-dibromocyclohexane with quinoline.

The condensation of propargyl aldehyde with diene hydrocarbons was carried out in sealed glass tubes in toluene solution at 115° for 2-4 hours, and in the case of cyclopentadiene at room temperature. The reaction products were distilled under vacuum.

The hydrazine derivatives of the hydroaromatic aldehydes were prepared in the usual way: the semicarbazones in aqueous methyl alcohol, p-nitrophenyl- and 2,4-dinitrophenylhydrazones in glacial acetic acid.

The reaction between the hydroaromatic aldehydes and the organo magnesium compounds was also carried out in the usual way. The mixtures were resolved with the aid of magnesium chloride.

The dehydration was carried out in a small Favorsky flask. The hydrocarbons formed were distilled over sodium.

Unsaturated hydrocarbon impurities were removed from the aromatic hydrocarbons by the action of a solution of bromine in acetic acid followed by dilution of the mixture with water and distillation of the hydrocarbon in steam. The amount of unconsumed bromine gave an approximate indication of the unsaturated hydrocarbon content. It was

assumed in the calculations that 1 molecule of an unsaturated hydrocarbon takes 2 molecules of bromine. This was the relationship between these reagents established in a previous study [4].

Condensation of propargyl aldehyde with divinyl

From 21.6 g of propargyl aldehyde and 25 g of divinyl in 80 ml toluene, 35.4 g dihydrobenzaldehyde was obtained. The yield on the amount of propargyl aldehyde was 82%. B.p. 184-185° (750 mm). The other physical constants are given in Table 1.

32.60 mg sub.: 92.45 mg CO₂. 21.75 mg H₂O. 0.1540 g sub.: 17.3 g benzene; Δt 0.413°. Found %: C 77.39; H 7.47. M 108.4. C₇H₈O. Calculated %: C 77.74; H 7.47. M 108.3.

The substance forms a semicarbazone very readily. This consists of long colorless plates with truncated edges (from alcohol). The melting points of this semicarbazone and other hydrazine derivatives are given in Table 1.

25.20 mg sub.: 5.605 ml N₂ (24.5°, 752 mm). Found %: N 25.25. C₈H₁₁ON₃. Calculated %: N 24.86.

The p-nitrophenylhydrazone was recrystallized from alcohol. Short orange needles.

26.90 mg sub.: 4.057 ml N₂ (24.5°, 755 mm). Found %: N 17.19. C₁₅H₁₃O₂N₃. Calculated %: N 17.28.

The 2,4-dinitrophenylhydrazone consists of pale orange needles (from benzene). Its solubility in organic solvents is poor.

9.90 mg sub.: 1.686 ml N₂ (24.5°, 755 mm). Found %: N 19.41. C₁₅H₁₂O₄N₄. Calculated %: N 19.44.

After 1 g of dihydrobenzaldehyde was heated for 6 hours with 1 g of maleic anhydride, steam distillation of the reaction mixture gave 0.6 g of a substance with b.p. 80° (20 mm), d_4^{20} 1.0237 and n_D^{20} 1.5182. Thus, the constants of the substance were unchanged.

3 g of dihydrobenzaldehyde was heated for 1 hour with a small amount of sulfur under a reflux condenser. Distillation of the mixture gave benzaldehyde:

B.p. 177-178° (748 mm), d_4^{20} 1.0462, n_D^{20} 1.5462. Literature data [12]: b.p. 178.1°, d_4^{20} 1.0498, n_D^{20} 1.5464.

This substance gave a p-nitrophenylhydrazone characteristic for benzaldehyde, with m.p. 193°, which did not depress the melting point of p-nitrophenylhydrazone from pure benzaldehyde. Considerable depression was produced when the original aldehyde was mixed with p-nitrophenylhydrazone.

5.5 g of dihydrobenzaldehyde was oxidized with silver oxide (prepared from 10 g AgNO₃) by heating on a water bath. A little alkali was then added to the solution. The filtered liquid was acidified with 25% H₂SO₄ and the organic acid was extracted by ether in an extractor fitted with a stirrer; this gave 1.8 g of a crystalline acid m.p. 112-113 (from water). It formed colorless plates. The substance contained about 65.8% carbon and 5.4% hydrogen. The molecular weight was about 256. It was not examined further.

From 16.2 g of dihydrobenzaldehyde and a solution of methylmagnesium iodide prepared from 4.3 g magnesium, 15 g (80%) of the corresponding alcohol was prepared. Its constants are given in Table 2. A test with p-nitrophenylhydrazine showed the absence of carbonyl compounds as impurity.

31.50 mg sub.: 88.95 mg CO₂; 27.35 mg H₂O. Found %: C 77.06; H 9.72. C₈H₁₂O. Calculated %: C 77.37; H 9.74.

The alcohol was dehydrated in 2.7 g portions by various methods, described in the general section of this paper. In all cases about 70% yield of the same product was obtained, with b.p. 134-136°, d_4^{20} 0.8694-0.8698, n_D^{20} 1.4990-1.5000.

After being heated with maleic anhydride or hydrochloric and acetic acids, and also after bromination in acetic acid, the remaining hydrocarbon (usually about 80% of the original) had physical constants which practically did not differ from the constants for ethylbenzene given in the literature:

B.p. 135-136°, d_4^{20} 0.8652, n_D^{20} 1.4958.

Literature data for ethylbenzene [13]: b.p. 136.2°, d_4^{20} 0.8670, n_D^{20} 1.4959.

From the amount of bromine used (0.19 g) for the bromination of a sample of the substance (1.0 g), its unsaturated hydrocarbon content was about 8%. The bromide isolated from acetic acid was crystallized out. It was not studied further.

Another alcohol was obtained from 5.5 g of dihydrobenzaldehyde, 1.4 g of magnesium, and 9 g of ethyl bromide. The yield was 74%.

33.17 mg sub.: 94.95 mg CO₂; 30.30 mg H₂O. Found %: C 78.11; H 10.22. C₉H₁₄O. Calculated %: C 78.23; H 10.21.

Dehydration of this alcohol by p-toluene sulfonic acid gave a hydrocarbon with b.p. 155-156°, d₄²⁰ 0.8632, n_D²⁰ 1.5010.

Its treatment with bromine solution in acetic acid gave propylbenzene with b.p. 158-159°, d₄²⁰ 0.8628, n_D²⁰ 1.4926.

The following constants are given for propylbenzene in the literature [13]: b.p. 159.2°, d₄²⁰ 0.8620, n_D²⁰ 1.4920.

From the amount of bromine used for bromination (0.38 g per 0.8 g hydrocarbon) the unsaturated hydrocarbon content in the original product was about 24%.

Condensation of propargyl aldehyde with diisopropenyl

6.5 g of the aldehyde and 10 g of diisopropenyl gave 12.5 g (73%) of dimethyldihydrobenzaldehyde, with the physical constants shown in Table 1.

52.35 mg sub.: 152.45 mg CO₂; 41.10 mg H₂O. Found %: C 79.47; H 8.79. C₉H₁₂O. Calculated %: C 79.37; H 8.88.

The semicarbazone consisted of colorless long plates with gladiate edges. It was recrystallized from aqueous alcohol.

16.90 mg sub.: 3.273 ml N₂ (26.5°, 748 mm). Found %: N 21.72. C₁₀H₁₅O₂N₃. Calculated %: N 21.75.

The p-nitrophenylhydrazone was recrystallized from benzene. It formed pale orange crystals.

20.78 mg sub.: 2.764 ml N₂ (25°, 748 mm). Found %: N 15.00. C₁₅H₁₇O₂N₃. Calculated %: N 15.49.

The 2,4-dinitrophenylhydrazone was recrystallized from benzene. It formed long orange needles.

24.70 mg sub.: 3.842 ml N₂ (22.5°, 750 mm). Found %: N 17.73. C₁₅H₁₇O₄N₄. Calculated %: N 17.71.

From 6.8 g of dimethyldihydrobenzaldehyde and the appropriate amount of Grignard reagent 6.5 g of a mixture of an alcohol and a ketone was obtained. The greater part of the substance boiled at 126-128° (20 mm), d₄²⁰ 0.9705, n_D²⁰ 1.5085. All fractions of the substance gave a positive reaction with p-nitrophenylhydrazine.

13.55 mg sub.: 39.15 mg CO₂; 12.40 mg H₂O. Found %: C 78.85; H 10.24. C₁₀H₁₄O. Calculated %: C 78.90; H 10.59.

The mixture was distilled with 10% solution of oxalic acid without previous separation. The hydrocarbon formed had b.p. 187-189°, d₄²⁰ 0.8730, n_D²⁰ 1.5030.

After it was treated with bromine as described above, its physical constants practically did not differ from those given in the literature for 1,2-dimethyl-4-ethylbenzene:

B.p. 187-189°, d₄²⁰ 0.8750, n_D²⁰ 1.5040.

Literature data [13]: b.p. 189.5°, d₄²⁰ 0.8741, n_D²⁰ 1.5032.

The unsaturated hydrocarbon content in the original substance, from bromination data, was about 17%.

Condensation of propargyl aldehyde with cyclopentadiene

From 15 g of the aldehyde and 20 g of cyclopentadiene, 16.5 g (50%) of endomethylenedihydrobenzaldehyde and 12.5 g of a tarry residue were obtained.

40.30 mg sub.: 117.25 mg CO₂; 24.70 mg H₂O. Found %: C 79.40; H 6.86. C₈H₈O. Calculated %: C 79.97; H 6.73.

All hydrazine derivatives of endomethylenedihydrobenzaldehyde should be prepared from cold solutions. Otherwise resinification takes place. On heating, they char and therefore they do not have sharp melting points.

The p-nitrophenylhydrazone was recrystallized from aqueous alcohol.

15.85 mg sub.: 2.274 ml N_2 (23°, 755 mm). Found %: N 16.55. $C_{14}H_{13}O_2N_3$. Calculated %: N 16.46.

The 2,4-dinitrophenylhydrazones forms red crystals.

8.0 g of endomethylenedihydrobenzaldehyde and Grignard reagent (from 1.9 g of magnesium) gave 6.2 g (70%) of an alcohol. The substance did not give the reaction of a carbonyl compound.

32.60 mg sub.: 94.60 mg CO_2 ; 25.70 mg H_2O . Found %: C 79.19; H 8.82. $C_9H_{12}O$. Calculated %: C 79.37; H 8.88.

It did not prove possible to obtain a hydrocarbon from this alcohol by dehydration with toluene sulfonic acid or by distillation with 10% oxalic acid solution, as resinification took place. This requires special study.

Condensation of propargyl aldehyde with cyclohexadiene

5.2 g of propargyl aldehyde, 12 g of cyclohexadiene-1,3, and 30 ml of toluene were heated together for 4 hours at 115°. The tubes were cooled to -80° before being opened. A considerable pressure was found during the opening. The gas evolved was partially passed into bromine. After removal of excess bromine by sodium bisulfite, a liquid with the properties of 1,2-dibromoethane remained:

B.p. 130-132°, n_D^{20} 1.5380.

Literature data [14]: b.p. 131.7°, n_D^{20} 1.5379.

Distillation of the liquid part of the reaction mixture under vacuum, and then under normal pressure, gave benzaldehyde as the only reaction product:

B.p. 177.5-178.5°, (745 mm), d_4^{20} 1.0460, n_D^{20} 1.5462.

The p-nitrophenylhydrazone had b.p. 192°.

SUMMARY

1. The homocyclization reaction of divinyl, diisopropenyl, cyclopentadiene, and cyclohexadiene with propargyl aldehyde was studied.
2. It was established that in every instance except the last the reaction products are dihydrobenzaldehyde or its analogs.
3. When cyclohexadiene reacts with propargyl aldehyde, the reaction products are ethylene and benzaldehyde.
4. It was shown that when dihydrobenzaldehyde is heated with sulfur it undergoes dehydrogenation and forms benzaldehyde.
5. A series of secondary alcohols was synthesized by the action of Grignard reagents on the hydroaromatic aldehydes obtained.
6. It was shown that the above secondary alcohols mainly form aromatic hydrocarbons when dehydrated under various conditions.

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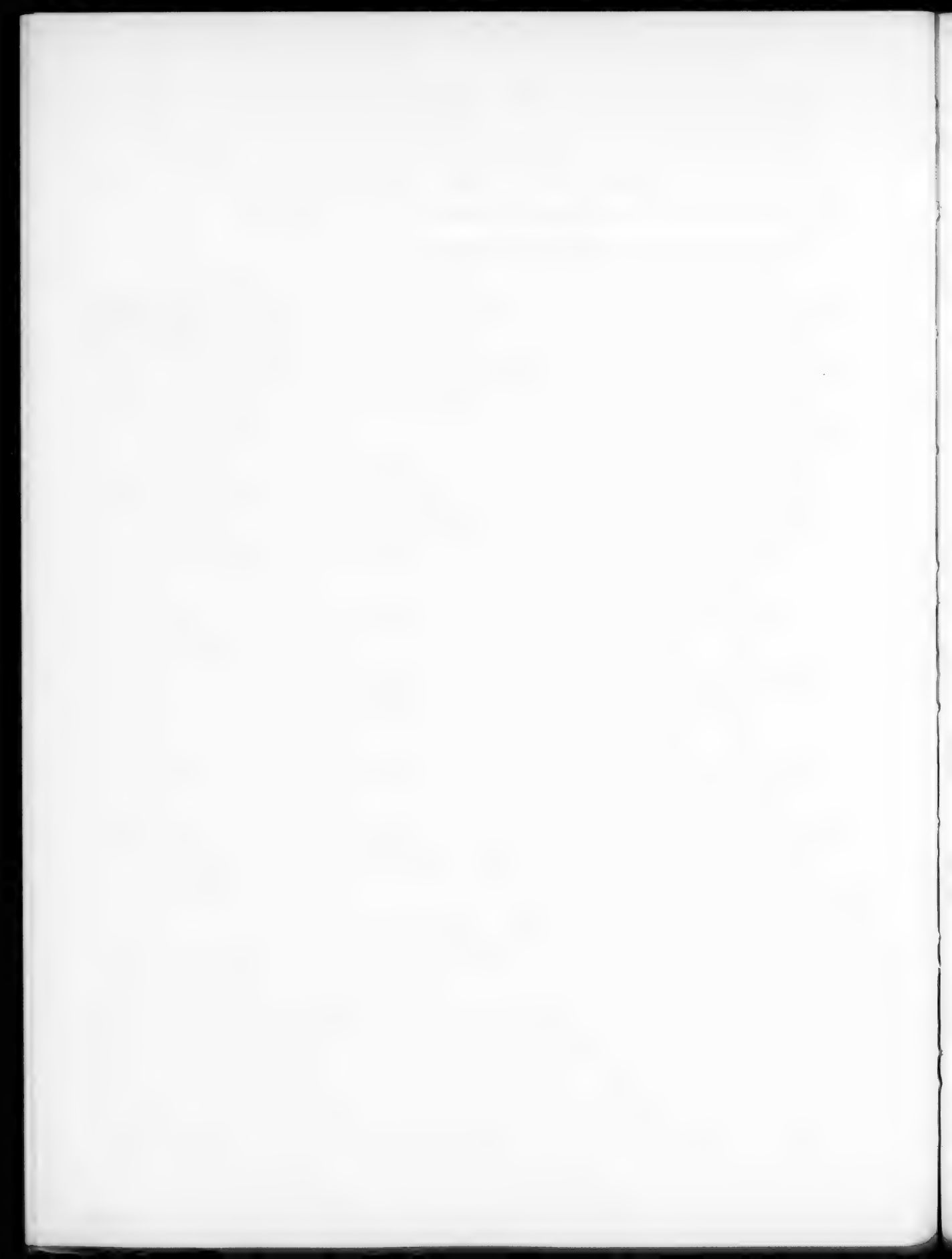
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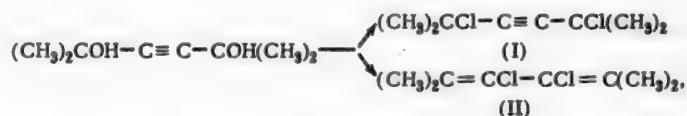


THE ACTION OF CONCENTRATED HYDROCHLORIC ACID ON TETRAMETHYLBUTYNE DIOL. II

A. I. Zakharova and G. D. Ilina

In a previous paper on the action of concentrated hydrochloric acid on tetramethylbutyne diol, one of the present authors [1] showed that two dichlorides are formed in this reaction, with b.p. 65-67° and 80-82° at 15 mm. Difficulties were met in attempts to prove the structure of these dichlorides. It did not prove possible to oxidize the dichlorides by alkaline permanganate solution. At ordinary temperatures the dichlorides were not oxidized, while on heating no oxidation products could be isolated, due to the fact that it became sufficiently evident that in these conditions they were oxidized further to CO₂ and H₂O, but the greater portion of the dichlorides remained unchanged. A noticeable reaction started by the action of metallic sodium on the dichlorides in ether solution, and the dichloride with b.p. 65-67° at 15 mm reacted more vigorously. Chlorine was evidently split off and an unsaturated hydrocarbon was formed, but the latter polymerized in the presence of sodium. The dichloride with b.p. 80-82° at 15 mm did not react with zinc dust in an alcohol medium at all, while its isomer with b.p. 65-67° at 15 mm partly reacted, but the primary product formed could not be isolated, as it was converted into a polymer.

The structure of the dichlorides could not be determined with certainty from these studies. On the assumption that the reaction between acetylene glycol and concentrated hydrochloric acid proceeds according to the equation:



we presumed that the dichloride with b.p. 65-67° at 15 mm had the diene structure, and the dichloride with b.p. 80-82° at 15 mm was the acetylenic derivative.

Recently R. Ya. Levina and Yu. S. Shabarov [2], with the aim of reacting the ditertiary acetylenic dichloride (I) with an organomagnesium compounds, synthesized both the dichlorides prepared by us, and to prove their structure they used the reaction discovered and developed for the acetylenic monochlorides by T. A. Favorskaya. The latter showed in a number of papers [3] that tertiary acetylenic monochlorides are isomerized into diene derivatives by the action of cuprous chloride and ammonium chloride in an acid medium. R. Ya. Levina and Yu. S. Shabarov subjected the dichloride with b.p. 65-67° at 15 mm to this treatment, and converted 73% of it to the higher boiling dichloride with b.p. 80-82° at 15 mm. On the basis of this result, and also because the higher boiling dichloride did not react with the organo-magnesium compound even upon prolonged heating, these authors concluded that the dichloride with b.p. 65-67° at 15 mm has an acetylenic structure, while the dichloride with b.p. 80-82° at 15 mm is a diene derivative.

Even before the publication of the paper by R. Ya. Levina and Yu. S. Shabarov we decided to return to the question of the proof of the structure of the dichlorides obtained by the action of concentrated hydrochloric acid on tetramethylbutyne diol, by the use of the combinational light-scattering method. It was found that the spectrum of the dichloride with b.p. 65-67° at 15 mm had a strong line which corresponded to the characteristic frequency of the triple bond - 2235 cm⁻¹. No lines were observed in the frequency region characteristic of the double bond. The combinational light-scattering spectrum of the dichloride with b.p. 80-82° at 15 mm contained lines with characteristic frequencies of 1626 and 1666 cm⁻¹, which is evidence of the presence of a double bond in the compound; characteristic triple bond frequencies were absent.

Thus, the results of a spectrographic study of the dichlorides showed, in agreement with the findings of Levina and Shabarov, that the dichloride with b.p. 65-67° at 15 mm should be attributed to the structure of an acetylenic derivative, 2,5-dichloro-2,5-dimethylhexyne-3 (I), while the dichloride with b.p. 80-82° at 15 mm has a diene structure, 3,4-dichloro-2,5-dimethylhexadiene (II).

Before the spectrographic investigation the dichlorides were carefully fractionated and then subjected to 3-fold molecular distillation. It is interesting to note that the dichloride with b.p. 65-67° at 15 mm was obtained in the crystalline state (m.p. 28-29°). Evidently, in this case the dichlorides had been most thoroughly separated*.

The starting glycol - tetramethylbutyne diol - was prepared by A. E. Favorsky's method, by condensation of acetone with acetylene in presence of powdered KOH in ether. The method of carrying out this reaction as used by A. T. Babayan was somewhat modified (see Experimental Section), which made it possible to increase the glycol yield to 80% (instead of 60% [5]). The reaction between concentrated hydrochloric acid and the glycol was carried out in conditions described in a previous paper [1], with the difference that the reaction was carried out with cooling in order to retard the isomerization of the acetylenic to the diene dichloride.

EXPERIMENTAL

Preparation of 2,5-dimethylhexyne-3-diol-2,5. 300 g of powdered caustic potash and 700 ml of dry ether were placed in a thick-walled flask fitted with a rapidly rotating blade stirrer, reflux condenser, and dropping funnel. The mixture was saturated with acetylene for 1 hour while being cooled and stirred. 87 g (1.5 moles) of freshly distilled acetone was added drop by drop for one and a half hours (with a continuous stream of acetylene), after which the stream of acetylene was stopped and another 87 g of acetone was quickly added. The reaction mixture was thoroughly stirred and left 48 hours. After cooling, the reaction mixture was hydrolyzed by water, the ether layer was washed with water, a current of CO₂ was passed through it for 2 hours, and it was dried with potash. After removal of the ether, unreacted acetone, and the acetylenic alcohol, the glycol was redistilled in a vacuum from a flask with a sword-shaped outlet. M.p. 95-97°. The yield was 170 g (80%) calculated on the acetone used for the reaction.

Action of concentrated hydrochloric acid on tetramethylbutyne diol. 284 g (2 moles) of the glycol and 1.5 liters of concentrated hydrochloric acid (d 1.19) were stirred in a round bottom flask for 4 hours with cooling. The dark oily upper layer was separated off, washed with water, and dried with calcium chloride. Two fractions were isolated after fractionation:

1st b.p. 65-67° at 15 mm, 109 g (30.4% on the glycol taken). M.p. 28-29°, n_D^{20} 1.4613, d_4^{20} 1.0118, MR_D 48.58. C₈H₁₂Cl₂ \bar{F} Calc. 46.86.

2nd b.p. 80-82° at 15 mm, 195 g (54.4%), n_D^{20} 1.4940, d_4^{20} 1.0556, MR_D 49.39. C₈H₁₂Cl₂ \bar{F}_2 . Calc. 47.94.

Combinational light-scattering spectrum of 2,5-dichloro-2,5-dimethylhexyne-3 (I):

234 (2), 338 (2), 421 (1), 464 (1), 577 (4), 607 (4), 701 (5), 846 (3), 918 (3), 1113 (3), 1165 (2), 1208 (1), 1446 (2), 2235 (9), 2295 (2).

Combinational light-scattering spectrum of 3,4-dichloro-2,5-dimethylhexadiene-2,4 (II).

193 (1), 261 (1), 344 (3), 414 (3), 468 (3), 517 (5), 773 (3), 1031 (1), 1170 (3), 1245 (1), 1375 (4), 1437 (4), 1626 (4), 1666 (10).

SUMMARY

It was established by studies of the combinational light-scattering spectra of the two isomeric dichlorides obtained by the action of concentrated hydrochloric acid on tetramethylbutyne diol that the dichloride with b.p. 65-67° at 15 mm has an acetylenic structure - 2,5-dichloro-2,5-dimethylhexyne-3 (I), while the dichloride with b.p. 80-82° at 15 mm is a diene derivative, 3,4-dichloro-2,5-dimethylhexadiene-2,4 (II).

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* Dupont [4], who studied the action of hydrogen chloride on tetramethylbutanediol, obtained one dichloride, with b.p. 62-63° at 15 mm, m.p. 29°. He attributed an acetylenic structure to the dichloride.

INVESTIGATIONS OF COMPOUNDS CONTAINING THREE-MEMBERED OXIDE RINGS

XII. REACTION OF THE ETHYL ESTER OF β,β' -DIETHYL- AND OF THE ETHYL ESTER OF β,β' -DIPROPYLGLYCIDIC ACID WITH ANILINE

V. F. Martynov and V. F. Martynova

As the result of earlier investigations of the reaction between β -disubstituted glycidic acid and aromatic amines [1-5], it was possible to determine the point of rupture of the epoxy ring of glycidic acids and also to develop a new method for the synthesis of indole homologs. The aim of the present study was to investigate the possibilities of this new method of synthesizing the indole structure.

The present general methods for the preparation of indole homologs all have the same general defect: with their aid it is very difficult or quite impossible to synthesize indole derivatives containing radicals more complex than methyl at the 2nd and 3rd carbon atoms.

For example, the method of Fischer [6], which is the most widely known in the literature, is unsuitable in principle for the preparation of such compounds. Indoles are produced by this method by the decomposition of aryl hydrazones of aldehydes, ketones and α -ketonic acids; if it is desired to obtain indoles with substituents at the 2nd and 3rd carbon atoms, the starting substances are usually ketone aryl hydrazones, but indoles of known structure can then only be formed if one of the ketone radicals is a methyl. Closure of the indole ring takes place by the utilization of the carbon atoms of the larger radical. If both radicals should contain several carbon atoms, the synthesis of indoles of a definite structure is impossible, since this rule has not been proved to be generally applicable and it has no definite basis. In such a case the reaction may take two different courses.

The second general method for synthesis of the indole ring with aryl amino ketones as starting materials [7-8], suffers from almost the same defect as Fischer's method. Here the syntheses can be easily effected only on the basis of ketones which contain two or one methyl groups as their radicals, because otherwise the preparation of the corresponding aryl amino ketones is very difficult. The reason for this is that aryl amino ketones are usually synthesized from α -halo ketones, which can be synthesized easily only from ketones which contain, as indicated above, at least a methyl group linked to the carbonyl. If the carbonyl group is linked to radicals containing several carbon atoms, as in ethyl propyl ketone, the synthesis of α -halo ketones of a definite structure becomes very complicated. Similar difficulties arise also in the third method, in which indoles are prepared by intramolecular Claisen condensation of ortho-acyl or ortho-aryl derivatives of alkyranilines [9, 10].

The acyl derivatives of o-toluidine are readily available, but ortho-alkyl substituted anilines containing several carbon atoms in the radical are difficult to obtain, and indoles containing substituents at the 2nd and 3rd carbon atoms can be obtained only from these.

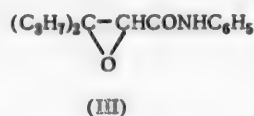
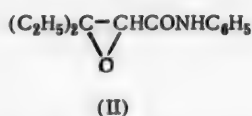
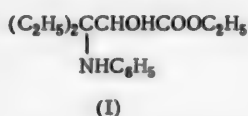
It therefore appeared of interest to investigate the possibilities of the new method of indole ring synthesis for the preparation of 2,3-diethyl- and 2,3-dipropylindoles.

According to our scheme for the conversion of the ethyl esters of α -hydroxy- β -aryl amino acids into indole homologs [1-5], in this case it was necessary to start with the ethyl esters of β,β' -diethyl- and β,β' -dipropylglycidic acids by the addition of aniline at the epoxy ring. It was, of course, to be expected that opening of the epoxy ring of these glycidic acids by the action of aniline would occur with great difficulty because of the protective shielding action of the alkyl groups. In fact, the ethyl ester of β,β' -diethylglycidic acid proved to be very resistant to the action of aniline. When a mixture of aniline was heated with the glycidic ester for 23 hours at 170-180°, the yield of the reaction product, the ethyl ester of α -hydroxy- β -ethyl- β -anilinovaleric acid (I) was only 17%. An attempt was made to increase the yield by raising the reaction temperature, but a new difficulty arose — some new crystalline compound began to be formed, the amount of which increased with rise of temperature and

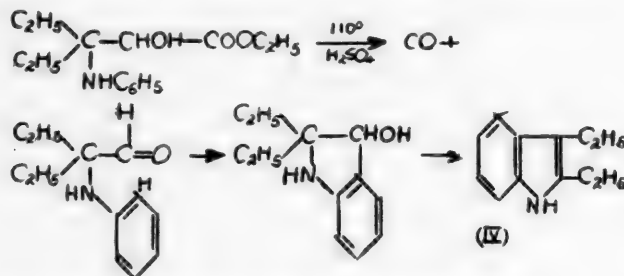
the time for which the reaction mixture was heated. Eventually, when the reaction was carried out in a flask under a reflux condenser with the reaction mass at the boil, only the crystalline product was obtained. Analysis of this compound suggested that it was the anilide of β,β' -diethylglycidic acid (II).

Evidently, at temperatures above 180° , the reaction between aniline and the ethyl ester of β,β' -diethylglycidic acid proceeds in two directions, with the formation of an addition product at the epoxy group, and of the anilide of the original glycidic acid. Above a definite temperature, the latter reaction apparently predominates. The substitution of the ester group by the anilide group proceeds much more rapidly than the opening of the epoxy ring.

The epoxy ring in the ethyl ester of β,β' -dipropylglycidic acid was even more resistant to aniline. The expected addition product was not obtained when a mixture of these substances was heated at 180 – 185° . The reaction was then carried out as in the preceding instance, with the reaction mixture at the boil; the reaction product was then obtained in the form of a crystalline compound. Investigation showed that this was an anilide. Thus, in the ethyl ester of β,β' -dipropylglycidic acid steric hindrance becomes so great that the epoxy ring completely loses its reactivity to aniline, and the only reaction product is the anilide of β,β' -dipropylglycidic acid (III).



The addition product of aniline and the ethyl ester of β,β' -diethylglycidic acid, the ethyl ester of α -hydroxy- β -ethyl- β' -lanilinovalerianic acid, was treated with concentrated sulfuric acid on heating. At 110° , as in all the other cases, vigorous evolution of carbon monoxide took place. The other fragment of the molecule could only be 2,3-diethylindole (IV), the formation of which can be represented by the following scheme:



The analytical data of our product completely agreed with diethylindole.

It must be pointed out that the possibility of synthesizing 2,3-diethylindole has been discussed in the literature by A. E. Arbuzov and his co-workers [11]. Their starting material was ethyl propyl ketone phenylhydrazone. The catalytic decomposition of this compound in presence of cuprous chloride gave a compound which, by its analytical data, could have been either 2,3-diethylindole or 2-propyl-3-methylindole. These authors could not, of course, decide on one or the other of these formulas, since the formation of either compound can be considered as equally probable. They claimed, however, that they prepared a single definite compound, and not a mixture of the two possible substances. By a comparison of certain physical constants, for example, the melting points of the picrates of their compound (144°) and of ours (122°), it can now be said that these authors prepared 2-propyl-3-methylindole by the decomposition of the phenyl hydrazone of ethyl propyl ketone.

Thus, the opinion sometimes expressed in the literature that in the indole synthesis by Fischer's method the larger radical participates in the formation of the pyrrole ring is not a general law.

EXPERIMENTAL

Synthesis of the ethyl ester of α -hydroxy- β -ethyl- β' -anilinovalerianic acid. A mixture of 17 g (0.1 mole) of the ethyl ester of β,β' -diethylglycidic acid and 27 g (3 moles) of freshly distilled aniline was sealed in a bulb which was heated for 23 hours at 170 – 180° . The reaction mixture turned slightly yellow, and a slight pressure increase was noted when the bulb was opened. Vacuum distillation yielded 5 g (17%) of a yellowish thick liquid, b.p. 165 – 167° (3 mm).

0.1051 g sub.: 5 ml N₂ (20°, 764 mm). Found %: N 5.40. C₁₅H₂₃O₃N. Calculated %: N 5.20.

Synthesis of the anilide of β,β' -diethylglycidic acid. A mixture of 17 g (0.1 mole) of the ethyl ester of β,β' -diethylglycidic acid and 27 g (3 moles) of freshly distilled aniline was heated to boiling under a reflux condenser on molten Wood's alloy for 10 hours. Vacuum distillation yielded 11 g of a straw-yellow very thick liquid which crystallized rapidly. Repeated crystallization from ligroine gave white scaly crystals, m.p. 114-115°.

0.0873 g sub.: 4.9 ml N₂ (25°, 755.5 mm). Found %: N 6.26. C₁₉H₁₇O₂N. Calculated %: N 6.40.

Synthesis of 2,3-diethylindole. 3.9 g of the ethyl ester of α -hydroxy- β -ethyl- β -anilinovalerianic acid was mixed with 15 ml of concentrated sulfuric acid. The reaction mixture was heated over an open flame with stirring. At 100°, bubbles of carbon monoxide began to come off, and at 115° this evolution became very vigorous. The temperature was not raised above 120°. When the gas evolution ceased, the dark reaction mixture was poured into ice, when a brown emulsion separated out. The sulfuric acid was neutralized by alkali, and the whole contents were distilled in steam. The emulsion in the distillate was extracted with ether, and after drying and removal of ether, 1.7 g (68%) of 2,3-diethylindole, of a pale yellow color, was obtained. The crude diethylindole was distilled under vacuum at 118-120° (2 mm). It was a greenish-yellow liquid. The picrate was in the form of yellow needles; it separated out only on dilution with water; m.p. 121-122° after recrystallization from 50% alcohol:

d_4^{20} 1.0205, n_D^{20} 1.5806, M_{rD} 56.46; calc. 54.95; EMR_D 1.51.

0.1187 g sub.: 8.5 ml N₂ (20°, 765 mm). Found %: N 8.38. C₁₂H₁₅N. Calculated %: N 8.09.

Synthesis of the ethyl ester of β,β' -dipropylglycidic acid. The synthesis was carried out by Darzens' method [12]. To a mixture of 57 g of dipropyl ketone (0.5 mole) and 61 g (0.5 mole) of ethyl monochloroacetate, sodium ethylate (0.5 mole) was added with cooling, so that the temperature did not rise above 0°. After the usual treatment, 40 g (40%) of the ethyl ester of β,β' -dipropylglycidic acid was isolated:

b.p. 108-110° (10 mm), d_4^{20} 0.9573, n_D^{20} 1.4337, M_{rD} 54.44; calc. 54.23.

0.1141 g sub.: 0.2771 g CO₂; 0.1045 g H₂O. Found %: C 66.20; H 10.17. C₁₁H₂₀O₃. Calculated %: C 66.0; H 10.00.

Synthesis of the anilide of β,β' -dipropylglycidic acid. 30 g of the ethyl ester of β,β' -dipropylglycidic acid in a mixture with 60 g of freshly distilled aniline (1:3) was heated to boiling on Wood's alloy under a reflux condenser for 45 hours. After 2-fold vacuum distillation, 8 g (20%) of a golden-yellow, viscous liquid, b.p. 151-152° (0.5 mm) was isolated. On the next day the substance crystallized out; recrystallization from petroleum ether gave silky needles, m.p. 52-53°.

0.0597 g sub.: 3 ml N₂ (28°, 764 mm). Found %: N 5.40. C₁₅H₂₁O₂N. Calculated %: N 5.16.

SUMMARY

1. The reactions of aniline with the ethyl ester of β,β' -diethylglycidic acid and the ethyl ester of β,β' -dipropylglycidic acid were studied.
2. It is shown that with the ethyl ester of β,β' -diethylglycidic acid the reaction proceeds in two directions: the addition of aniline at the epoxy ring, with the formation of the ethyl ester of α -hydroxy- β -ethyl- β -anilinovalerianic acid, and substitution of the ethoxy group by an aniline residue, with the formation of the anilide of β,β' -diethylglycidic acid. The reaction between the ethyl ester of β,β' -dipropylglycidic acid and aniline proceeds in one direction only, with substitution of the ester group by an anilide group, to form the anilide of β,β' -dipropylglycidic acid.
3. The conversion of the ethyl ester of α -hydroxy- β -ethyl- β -anilinovalerianic acid to 2,3-diethylindole has been effected.

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STUDY OF THE REACTION FOR THE CONVERSION OF DIACETONE-2-KETO-L-GULONIC ACID HYDRATE INTO L-ASCORBIC ACID IN ALCOHOL-FREE ORGANIC SOLVENTS

V. I. Veksler and G. E. Shaltyko

Of the many methods for the preparation of L-ascorbic acid (AA) from the hydrate of diacetone-2-keto-L-gulonic acid (HDAKGA), the one most widely studied is in which the reaction is carried out in organic solvents in presence of alcohols [1, 2]. Berezovsky and Strelchunas found that this method gives high yields of AA [2, 3]. They showed that in alcohol-containing mixtures the reaction passes through the stage of formation of an ester of 2-keto-L-gulonic acid, which is converted into AA [3]. The reaction has not been widely studied in organic solvents in absence of alcohols: there are patents [4] and also the results of Berezovsky and Strelchunas, who showed that in a dry inert solvent (chloroform, dichloroethane) the reaction does not take a definite course [2]. It might be thought that the lack of success with the use of inert solvents without addition of alcohols is primarily caused by the slight solubility of hydrogen chloride, which catalyzes the reaction [5, 6], in these solvents.

Our aim was to study the course of the reaction in organic solvents with the addition of substances which are not alcohols by their chemical nature, but which are capable of dissolving approximately the same amounts of hydrogen chloride as are alcohols. It is known that, in addition to alcohols, ethers are good organic solvents for hydrogen chloride [5, 6, 7]. In view of the need to use relatively high-boiling substances, dioxane and dibutyl ether were chosen from this group of compounds. It was confirmed experimentally that these substances are good solvents for hydrogen chloride. At room temperature, solutions were obtained containing 260 g and 146 g of hydrogen chloride in 1 liter of a mixture with dioxane and dibutyl ether respectively.

The study was performed by determinations of the yield of AA in reaction mixtures containing HDAKGA and dichloroethane, to which a solution of hydrogen chloride in dioxane or dibutyl ether was added. For comparison, a parallel experiment was simultaneously performed with a reaction mixture which contained, in addition to HDAKGA and dichloroethane, a solution of hydrogen chloride in 95% ethyl alcohol. The compared mixtures contained approximately equal amounts of hydrogen chloride. The mixtures were heated on a water bath at a definite temperature for 6, 6.5, and 9 hours. The results of the experiments are shown in the table.

It is seen from the results in the table that, as a rule, the yield of AA in all the experiments was higher in alcohol-containing mixtures than in mixtures containing dioxane or dibutyl ether as hydrogen chloride solvents.

The yield of AA is determined by the ratio of the rates of two processes: the formation and the decomposition of AA. We found that in the conditions studied there is no actual measurable decomposition of AA. Consequently, the results given in the table represent the relative rates of formation of AA in the reaction mixtures studied.

This difference of the rates of reaction in alcohol-containing and alcohol-free mixtures must be attributed to a different reaction mechanism. In alcohol-containing mixtures, an ester of 2-keto-L-gulonic acid, which is easily converted into L-ascorbic acid [1, 8] is decomposed; it is known, for example, that the methyl ester, in contrast to 2-keto-L-gulonic acid itself, is converted into AA in the living organism [9]. In alcohol-free mixtures, the 2-keto-L-gulonic acid itself and not its ester reacts, and this process is slower.

The different reaction mechanisms, and also the nature of the hydrogen chloride solvent, determine the formation of the reaction by-products. In alcohol-containing mixtures almost white AA is formed, free from tarry impurities. The mixtures containing dioxane give a dirty, tarry, sticky product. It is interesting to note that, according to Berezovsky and Strelchunas [2], a low yield of AA is obtained from dioxane solutions containing alcohol. In experiments in which hydrogen chloride in dibutyl ether was used, the AA was rather purer than in the case of dioxane. As the table shows, addition of water increases the reaction rate, which is in agreement with the findings of Berezovsky and Strelchunas, who demonstrated the favorable effect of water in alcohol-containing mixtures [3].

TABLE

Expt. No.	HDAKGA (g)	Dichloroethane (g)	Reaction conditions		Alcohol-containing mixtures				Alcohol-free mixtures				
			Bath temperature	Time (hours)	Hydrogen chloride solution			Yield of AA (as % of theoretical)	Hydrogen chloride solution			Yield of AA (as % of theoretical)	
					Amount (ml)	HCl content (g/liter)	Water content (%)		Solvent	Amount (ml)	HCl content (g/liter)		Water content (%)
1	20	40	75-76*	6	4	253	5	53.5	Dioxane	4	252	0	33.5
2	5	9.1	80-85	6	0.9	176	5	69	Dioxane	0.9	182	5.5	30.0
3	5	9.1	77-78	6	0.9	176	5	49.5	Dioxane	0.9	182	5.5	27.5
4	5	10	76-78	6	1	258	5	74.1	Dioxane	1	260	0	37.7
5	5	10	76-78	6	—	—	—	—	Dioxane	1	260	0	40.7
6	5	10	75-77	6	1	258	5	72.7	Dioxane	1	260	5	57.6
7	5	10	75-77	6	1	258	5	64.2	Dioxane	1	260	5	59.2
8	5	9	78-79	6.5	0.9	155	5	45.2	Dibutyl ether	1.0	146	5	41.2
9	10	20	70-71	9	2.0	155	5	67.5	Dibutyl ether	2.0	~160	0	17.8
10	10	20	70-71	9	2.0	155	5	69.5	Dibutyl ether	2.0	~160	0	29.1
11	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	10	28.2
12	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	10	25.4
13	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	25	71.5
14	10	20	70-71	9	—	—	—	—	Dibutyl ether	2.0	~160	25	49.2

EXPERIMENTAL**

Starting materials: Dioxane was distilled over metallic sodium, b.p. 99-101°, dibutyl ether was prepared from butyl alcohol [10], b.p. 139-142°, hydrogen chloride was dried by passing it through sulfuric acid, the HDAKGA was 98.5% pure (calculated as the hydrated substance).

Determination of the relative rate of formation of AA was carried out by heating of the reaction mixture on a water bath under a reflux condenser with vigorous stirring. The experiments with alcohol-free and alcohol-containing mixtures were carried out in parallel, under the same conditions. The yield of AA was determined by analysis of the reaction products by iodine titration in presence of starch. In most of the experiments the reaction product was separated by suction, thoroughly washed with a chloroform-alcohol mixture (4:1), dried, and analyzed. In some experiments the reaction mixture was analyzed direct without isolation or purification of the AA.

Determination of the rate of decomposition of AA. 0.1000 g samples of AA were heated for 6 hours on the water bath (76-78°) with a mixture of 1 ml of dichloroethane and 0.1 ml of hydrogen chloride solution in dioxane (260 g hydrogen chloride in 1 liter). After the heating, the amount of L-ascorbic acid was determined by iodine titration, and was 102.9 and 102.4% of the original amounts.

SUMMARY

It is shown that the conversion of the hydrate of diacetone-2-keto-L-gulonic acid into L-ascorbic acid is slower in mixtures in which ethers are used as solvents for hydrogen chloride than in alcohol-containing mixtures.

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**M. F. Galina and M. P. Benyamin participated in the experimental work.

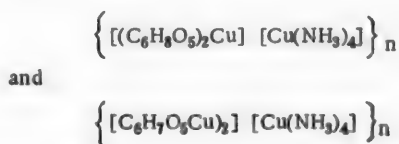


CHEMISTRY OF CUPRAMMONIUM SOLUTIONS OF CELLULOSE

VI. ALCOHOLATE COPPER ATOMS IN CUPRAMMONIUM SOLUTIONS OF CELLULOSE

S. N. Danilov and M. G. Okun

A number of studies [1, 2, 3] of cuprammonium and cupriethylenediamine solutions of polyhydric alcohols and cellulose led to the widespread acceptance of the view that cuprammonium solutions of cellulose contain the compounds:



A characteristic feature of these formulas is the presence of an anion containing copper atoms in alcoholate form, and a cation which is also linked in alcoholate structure to the cellulose, and which is a base, the copper tetramine complex. The interrelationships of copper, alkali, and Rochelle salt in Fehling's solution [1, 2] are often explained in terms of the copper alcoholate derivative of Rochelle salt.

The well-known precipitates formed by the action of caustic alkalis on cuprammonium solutions of cellulose, which are known in the literature as Normann's compounds [4], are given the composition: $(\text{C}_6\text{H}_7\text{O}_5)_2\text{CuNa}_2$ by analogy with the formula attributed [1] to sodium cupriglycerates: $(\text{C}_3\text{H}_5\text{O}_3\text{Cu})\text{Na} \cdot \text{H}_2\text{O}$. Hess and his co-workers [3] considered that if smaller amounts of caustic soda were added, cuprammonium solutions of cellulose might contain the compound $(\text{C}_6\text{H}_7\text{O}_5\text{Cu})\text{Na}$ (soluble). From their studies of the optical rotation of cuprammonium cellulose solutions they concluded that the angle of rotation (to the left) increases with increasing copper concentration and the subsequent increase in the concentration, of a copper-cellulose compound of high rotatory power in the solutions. The increase in the angle of rotation is particularly great if caustic soda is added to the cuprammonium solution of cellulose; the above-mentioned soluble copper-sodium cellulose derivative is then formed in the solution.

The existence of these compounds in cuprammonium solutions is confirmed, in the view of some authors, in addition to the above considerations, particularly by the experiments of Hess and Messmer [5] on the electrophoresis of cuprammonium solutions of cellulose and polyhydric alcohols.

These authors found that without addition of caustic soda to the solutions copper is apparently displaced only toward the cathode, and in presence of caustic soda, toward the anode. In their opinion, in absence of alkali the copper (the cellulose-copper anion) should also be displaced toward the anode. It is stated in their paper that in the anode limb of the electrophoresis cell cellulose separated out rapidly, which was explained by loss of copper from the anode space, as copper is displaced toward the cathode more rapidly than the anionic cellulose-copper complex is moved toward the anode. In the presence of caustic soda, the sodium ions are moved more rapidly toward the cathode, so that the complex ion is not decomposed and the transport of the copper-cellulose anion from the cathode becomes noticeable. They extended their experiments to solutions of glycerin, mannitol, sucrose, and other sugars, which are analogous to cellulose solutions, and obtained the same results throughout.

As electrolysis experiments are usually cited as proof of the presence of chemical compounds of the alcoholate type in cuprammonium solutions of cellulose, namely, an alcoholate copper atom in the anionic cellulosic part of the compound, it was important, for an understanding of the nature of cuprammonium solutions of cellulose, to make a closer study of the electrolysis (electrophoresis) of these solutions of cellulose and its derivatives, other sugars, and polyhydric alcohols.

Numerous electrolysis experiments were performed, first without separation of the anode and cathode spaces, and then with the use of a separating membrane, solutions of cupric hydroxide in ammonia being compared with cuprammonium solutions of cellulose, oxycellulose, methylcellulose, hydroxyethylcellulose, alginic acid, glucose,

sucrose, glycerol, sorbitol, and Fehling's solution. Ammonia solutions (15%) with and without caustic soda additions were used as the upper layer of electrolyte. In experiments with the apparatus in which the anode and cathode spaces were not separated, solutions of ammonia and a number of salts were used for the upper electrolyte layer, in order to raise the conductivity of the solution to the limits reached by the addition of caustic soda to the solution. Hess and Messmer assumed that movement of the liquid to the anode took place in presence of caustic soda. Our experiments showed that increase of the conductivity of the upper layer did not affect the phenomena which took place by the action of an electric current on cuprammonium cellulose solutions. It was found in all the experiments with different cuprammonium solutions that copper was deposited only on the cathode, there was no movement toward the anode, and no copper was found in the anode liquid.

It is therefore necessary to amend the conclusions drawn by Hess and Messmer. Our experiments on the action of an electric current on the solutions give reason to believe that cuprammonium solutions of polyhydroxy compounds do not contain alcoholate copper atoms in the presumed compounds.

The same conclusion must be drawn on the basis of our experiments on the action of ionites (anionites and cationites) on cuprammonium solutions of cellulose and other polyhydroxy compounds. Copper was taken up quantitatively by the cationites in all cases, while anionites produced no changes in the solutions. If, however, in agreement with the Traube-Hess hypothesis, cuprammonium cellulose solutions contained any at all stable cupricellulose anions, these might be expected to be taken up by the anionites.

Our results, which contradict the widely accepted [6] views of Traube and Hess, require other hypotheses to account for the interaction between the components of cuprammonium cellulose solutions.

In his determinations of the composition of cuprammonium cellulose compounds, K. Hess [3] attempted to prove the validity of the false hypothesis concerning the small cyclic molecules of high polymers. K. Meyer and H. Mark [7] considered these solutions in the light of their erroneous micellar hypothesis, which was persistently applied by T. Lieser [8] to account for the composition and properties of cuprammonium solutions of cellulose and the solution process itself, even after other workers [9] proved that they were molecular and not micellar in nature. In the work of one of the present authors [10] cuprammonium cellulose solutions were described as consisting of large cellulose molecules, which build up the cellulose fiber itself. The coagulation of the solutions by the action of salts was regarded as precipitation of cellulose in consequence of binding of the salt ions by the cuprammonium hydroxide, resulting in salting out of cellulose. Possibly, the salts coagulate the hydrophobic copper hydroxide, which is partly in the colloidal state. It was also doubted whether the sodium-copper precipitates (Normann) and cellulose cuprammonium compounds (Traube and Hess) have the composition ascribed to them in the literature.

Recently Arkhipov pointed out the unsatisfactory nature of the formulas in which alcoholate copper atoms are contained in the glucose residues in cellulose. In addition to the continuing studies of cuprammonium cellulose solutions by their rotation of the polarization plane (Arkhipov [11], Reeves [12]), other methods are also now in use (conductimetric [13], spectrophotometric, potentiometric [14]). However, the problem of the composition and structure of the presumed cuprammonium cellulose compounds has not yet been reliably solved. Different and often contradictory opinions have been put forward concerning the nature of cuprammonium cellulose solutions. According to some views [15], the solution of cellulose in ammoniacal copper hydroxide is a purely adsorptional process of colloidal peptization, but this reflects only one side of this complex phenomenon. Some authors [16] consider not only the copper amine complexes but also their compounds with cellulose to be complex compounds, but there are no adequate data or convincing analogies in support of this conclusion. Reeves [13] supports the view that cuprammonium hydroxide is added on to the glycol grouping of polyhydroxy compounds (carbon atoms 2 and 3 in the glucose residues of cellulose) but this requires more direct proof.

There is probably no special difference in principle between the reactions of cellulose with caustic soda and with cuprammonium hydroxide, the composition of which may be expressed by the formula $[\text{Cu}(\text{NH}_3)_m(\text{OH})_2]$, although it seems that in solutions the tetramine complex predominates, as was pointed out by D. P. Konovalov [17].

While cuprammonium hydroxide is a typical unstable complex base of variable composition, we believe it more probable that cellulose-cuprammonium compounds should be considered not as complexes but as molecular compounds, analogous to alkali compounds of cellulose: $[(\text{C}_6\text{H}_{10}\text{O}_5)_x(\text{NaOH})_y(\text{H}_2\text{O})_z]_n$ - for alkali cellulose, and $\{(\text{C}_6\text{H}_{10}\text{O}_5)_x - [\text{Cu}(\text{NH}_3)_m(\text{OH})_2]_y(\text{H}_2\text{O})_z\}$ - for the cuprammonium cellulose compound.

EXPERIMENTAL

The Experimental Section describes studies of the electrolysis (electrophoresis and electroosmosis) of cuprammonium cellulose solutions and (for comparison) of ammoniacal solutions of copper hydroxide, and also chromatographic investigations of the same solutions.

Starting substances and solutions. Cotton cellulose from a single batch with the following characteristics: alpha-cellulose 98%, as 0.3%, copper number 0.3, moisture 0.3. Oxycellulose was prepared by A. M. Nastyukov's method, by permanganate oxidation of cellulose and had: acid number — 27 and 31 ml of 0.01 N sodium hydroxide solution, copper number 10-20, carboxyl group content from 0.7 to 0.9%; it was easily ground to a powder. Methyl-cellulose, prepared from alkali cellulose by the action of dimethyl sulfate, contained 9.8-10.1% methoxyl groups. Hydroxyethylcellulose was prepared in the usual way from alkali cellulose in presence of ethylene oxide at -5° , and was isolated by precipitation by alcohol. Alginic acid was isolated from 10% aqueous sodium alginate solution by an alcoholic acetic acid solution, washed with alcohol, and dried in a vacuum.

Crystalline copper hydroxide, obtained from copper sulfate by the action of ammonia and caustic soda (by Peligot's method) was used in the experiments. Moist copper hydroxide was used. The copper content was determined electrolytically (a sample of 0.5-1 g of the hydroxide was dissolved in 25% sulfuric acid and a current of 3 A was passed for 40-60 minutes at 50° with vigorous stirring).

A weighed sample of the copper hydroxide was mixed with water in vessel of accurately determined size, a weighed amount of the cellulose and the other substances under investigation was added, and ammonia was then added rapidly, the whole capacity being used to displace the air. The liquid was then shaken for 1.5-2 hours. The solutions were separately prepared for each experiment and stored for one day.

The ratio of the components with which solution takes place is determined by the properties of the cellulose. The solution compositions for 0.5 to 4% by the properties of the cellulose and other polysaccharides were determined experimentally. For the preparation of more concentrated solutions, shaking alone is insufficient, and vigorous stirring is needed. The ammonia concentration in all the experiments was 15% of the weight of the solution. The complete dissolution of the cellulose and copper hydroxide was checked microscopically.

Excess ammonia was used for dissolving the copper hydroxide. There is no stoichiometric ratio between cellulose and copper in the solution: the higher is the cellulose concentration per unit volume of the solution, the lower is the relative concentration of copper required for solution to take place. Lower concentrations of copper are needed to dissolve oxycellulose, cellulose ethers, and alginic acid, than to dissolve cellulose.

1. Action of an electric current

Two series of experiments were carried out to determine the chemical nature of cuprammonium cellulose solution by use of the migration of charged particles and ions in an electric field: 1) electrophoresis in which the anode and cathode spaces were not separated from the solution under investigation; 2) electrophoresis with a separating membrane. Direct current at 110 V was used, and the current was varied between 30 and 200 mA.

1) Electrophoresis without separation of the anode and cathode spaces. As the determination was hindered in U-tubes without taps by some mixing of the layers, resulting in an indistinct separation boundary, apparatus of the following construction was used for the electrolysis: the tube was fitted with two taps with cross-sections equal to that of the tube limbs, and had, at its lower part, an upward branch with a tap for adding the solution for investigation; both limbs of the tube were graduated so that the rate of movement of the colored layer could be measured. As the passage of current heats the liquid considerably, thus causing the layers to mix rapidly, the apparatus was placed in a thermostat cooled by running water. The electrodes were platinum plates 5×30 mm, and 0.2 mm thick. To prevent mixing when the apparatus was filled, the solution of electrolyte was added to the limbs of the U-tube from above with the taps closed, and the platinum electrodes were then lowered in. The investigated solution was then gradually added through the branch tube, the taps were opened, and the electrolyte was displaced upwards until the electrodes were immersed in it. The duration of each experiment was 1 to 3 hours; water was also electrolyzed, and this was accompanied by evolution of gas bubbles on the electrodes. To prevent mixing of the liquid, the evolution of bubbles must be slow. The most typical of the numerous experiments are described.

a) In the first series of experiments the upper electrolyte layers was 15% ammonia solution, and, in parallel experiments, the same solution with the addition of 1% caustic soda per 100 parts of the ammonia solution (15%). The caustic soda was added to increase the hydroxyl ion content, because of the available data concerning sodium-cuprammonium cellulose complexes, of which the so-called Normann compounds are an example, and also because of the polarimetric investigations carried out by K. Hess and his co-workers on cuprammonium cellulose solutions in presence of caustic soda. The height of the layer of the investigated solution was 30 mm. The role of the caustic soda may be to increase the conductivity of the solution.

When 1% solution of ammoniacal copper hydroxide was used, which is presumed to contain copper ammine complexes, the current of electricity caused the colored mass of solution to move toward the cathode, where copper

was then deposited from the solution; no changes were observed in the anode limb, and the upper layer remained colorless. Both in this and in other experiments the presence of caustic soda in the upper layer of 15% ammonia solution mainly favored the disappearance of the boundaries between the layers in the cathode and anode spaces (by intensified electrolysis of water).

Similar effects accompanied the electrophoresis of 1% cuprammonium cellulose solution: the boundaries between the layers gradually became indistinct, especially in presence of caustic soda. When the cellulose concentration in the solution was increased (2.4%), the boundaries were retained longer, especially in absence of caustic soda, but the upper layer in the cathode space became blue without disappearance of the boundary between the layers, although the boundary rose by several millimeters; copper was deposited at the cathode. White flakes of cellulose (containing no copper) were deposited in the anode space at the boundary.

When 4% cellulose solution was used, in presence of caustic soda in the upper layer, the cellulose flakes which formed at the boundary slowly moved to the anode, but did not reach it even in experiments lasting many hours. The addition of 1% caustic soda solution (a total of 0.5 g caustic soda) to 2% cellulose solution did not change the observed effects, although the layers mixed more quickly.

The electrophoresis of hydrophilic cellulose ethers in such conditions was also studied, and also, to elucidate the role of carboxyl and hydroxyl groups, the electrophoresis of specimens of oxycellulose, alginic acid, Fehling's solution, sugars, and polyhydric alcohols. For example, it was found that the electrophoresis of 4% methylcellulose and hydroxyethylcellulose solutions (1.75% copper in the solutions) differed little from the experiments described above: copper was deposited at the cathode, the anode liquid turned blue, and, in the electrophoresis of hydroxyethylcellulose, in presence of caustic soda, flakes of hydroxyethylcellulose (free from copper) appeared at the boundary due to the solution becoming poorer in copper. Thus, no effects were observed which might prove the presence of copper in the anions of cuprammonium cellulose complexes.

In the electrolysis of cuprammonium solutions of oxycellulose, white flakes were deposited more rapidly in the anode limb, but these flakes also did not contain copper; no copper was deposited at the anode. The oxycellulose formed at the boundary between the two layers was retained at the boundary and then rose toward the anode without reaching it, but the boundary itself fell by 7 mm in 3 hours. When alginic acid was used, the liquid rose considerably in the anode limb and fell in the cathode limb (by 23 mm). The electrophoresis of 4% sodium alginate solution did not differ from the electrophoresis of the cuprammonium complex.

Solutions of tartaric acid in ammoniacal copper hydroxide solution or mixed with copper sulfate showed similar effects under the action of an electric current. Metallic copper was formed at the cathode, while the boundary between the solution moved toward the anode if the upper layer contained caustic soda. The same was observed in the electrolysis of Fehling's solution but the anode boundaries did not move. The experiments showed that movement of the solutions toward the anode was more pronounced when caustic soda was present in the upper layer, and particularly if the molecules of the substance contained carboxyl groups (as in oxycellulose); this is apparently caused by changes in the conductivity of the solutions and possibly to increased electric charge of the substance.

When an electric current acted upon cuprammonium solutions of glucose, sucrose, glycerol, and sorbitol, the colored solution easily diffused into the electrolyte, which may have been caused by the low viscosity of these solutions. The separation boundary between the solutions moved toward the cathode, where metallic copper was formed. These effects did not differ from those observed in ammoniacal solutions of copper hydroxide.

Thus, this series of experiments did not provide confirmation of the hypothesis put forward by Traube and Hess [2, 3] concerning the presence of alcoholate copper in cuprammonium solutions of polyhydric alcohols, sugars, cellulose and its ethers, oxycellulose, tartaric acid, and Fehling's solution.

b) In the second series of experiments (without separation of the anode and cathode spaces) a study was made of the part played by electrolytes in the solutions in relation to the addition of caustic soda, and in particular the role of electrical conductivity. The following were added to 15% ammonia solution in the upper layer: lithium hydroxide, as an analog of sodium hydroxide, but differing in the greater hydration of the lithium ion, in 2.5% concentration (conductivity $\kappa \cdot 10^4 = 1416$); 5% solution of potassium hydroxide ($\kappa \cdot 10^4 = 1464$); 5% solution of caustic soda, the conductivity of which is close to that of the above solutions ($\kappa \cdot 10^4 = 1954$). Salts were also used which could partially give up their anions to the ammine copper complex: 5% ammonium sulfate solution ($\kappa \cdot 10^4 = 552$), 5% lithium chloride solution ($\kappa \cdot 10^4 = 733$), 5% sodium chloride solution ($\kappa \cdot 10^4 = 672$), 15% ammonia solution ($\kappa \cdot 10^4 = 10$). Each electrophoresis experiment with cuprammonium cellulose solution (4% cellulose) and the various electrolytes was carried out three times, and the same effects were observed in each.

The experiments showed that increased conductivity of the solution by use of 15% ammonia solution with the above salt additions as electrolytes (from $\kappa \cdot 10^4 = 10$ for ammonia solution to $\kappa \cdot 10^4 = 700$ when the salts were added) did not result in any special changes in the action of the current on cuprammonium cellulose solution. The solution, as was the case when an ammoniacal electrolyte was used, moved a little in the direction of the cathode, where metallic copper was formed; the cathode liquid turned blue. Cellulose was formed in the anode limb, but the separation boundary remained stationary.

The effect of additions of caustic alkalis to 15% ammonia solution was rather different. In all the experiments in which alkalis were added the boundary rose in the anode limb, but without a corresponding fall of the boundary in the cathode limb. The liquid turned blue near the cathode, and metallic copper was formed at the cathode. The special effect of alkalis on the electrophoresis of cuprammonium solutions is apparently due to the hydroxyl ions of the alkalis and their high conductivity.

2) Electrophoresis with a separating membrane. In order to prevent diffusion of the solution into the upper layer of electrolyte, experiments were performed in which the anode and cathode spaces were separated by porous ceramic membranes with $1.83 - 2\mu$ pore diameter. The apparatus consisted of two porous ceramic beakers, one inside the other, placed in a small glass crystallizing dish. Various arrangements of electrode positions and ways of placing the electrolytes and test solutions into the three spaces — the central and the two annular — were investigated, as shown in the table.

The studies performed in porous vessels on ammoniacal copper hydroxide and cuprammonium cellulose solutions showed that the copper ammine complex passed freely through the porous walls with pore size of about 2μ , and metallic copper was deposited on the cathode, and that electrophoresis of cuprammonium cellulose solutions took the same course both in presence of ammoniacal electrolyte and after addition of caustic soda to the latter.

When cuprammonium cellulose solution was the anode liquid, cellulose was deposited on the walls of the porous vessel in the anode space, apparently as the result of decomposition of the ammine copper complex, as copper was formed on the cathode.

When the anode space was situated between porous walls, no cellulose appeared in the outer chamber in the anode space, even in traces, but it was deposited on the inner surface of the porous wall, while copper was deposited at the cathode, and there was some loss of the anode liquid. When the electrolyte was completely separated from the cuprammonium cellulose solution which was between the two porous walls, the cellulose particles did not penetrate through the porous walls of the vessels. These experiments also did not confirm the presence of copper in the anion of the cellulose complex.

II. Interaction between cuprammonium cellulose solutions and ionites

In order to obtain data which might help the clarification of the chemical nature of cuprammonium cellulose solutions, the ion exchange of such solutions on cationites and anionites was studied. If cuprammonium cellulose solutions contain compounds of cellulose with a cuprammonium complex base, and copper atoms participate in complex formation in the anionic and cationic parts of the molecule, such ions might be expected to be taken up by anionites and cationites. It is obviously necessary for both ions to have adequate stability and to be capable of being absorbed. Copper may be absorbed from solutions, for recovery purposes, by means of H-permutites and other cationites.

The following Wofatites were used in our experiments: the weakly acidic cationite C, the strongly acid cationites D and KS, the weakly basic anionites M, MP, MMG-1, TN, and the strongly basic anionite PEK, in static and dynamic conditions. In the static experiments, a weighed sample of the anionite was placed direct in the solution to be studied, from which the ions were to be removed, and the solution was shaken intermittently or continuously. In the dynamic experiments, the cationite or anionite was wetted with water and placed in a column 200 mm high and 20 mm diameter, with a porous bottom, and the solution was then added. In order to obtain an even layer of ionite in the column, it was sufficient to tap the walls. The cationites were washed with 50 ml of 12% hydrochloric acid, the first portions being passed in a fine jet and the rest drop by drop, and were then treated with 250 ml of 5% standard hydrochloric acid added dropwise. Periodic determinations of the acid were then made in samples (5-10 ml) to determine whether the cationite was ready for the experiment, when the concentration of the effluent acid was equal to that of the original acid. The anionites were washed with 50 ml of 12% soda, and then with 250 ml of 5% standard soda solution. The conditions of treatment were analogous to those for the cationites. The ionites prepared in this way were washed for a long time (3-4 days) with distilled water; the first portions of water were added in a fine jet, and the rest drop by drop. Methyl orange and phenolphthalein were used as indicators.

1 and 2% cuprammonium cellulose solutions, and, for comparison, 0.5 and 1% solutions of copper hydroxide in ammonia, were studied.

Electrophoresis with Separating Membrane

Experiment number	Arrangement of electrodes and liquids			Effects in the spaces	
	Central space	Inner ring	Outer ring	Cathode	Anode
1	Cathode - 15% ammonia solution	Solution of copper hydroxide in ammonia	Anode - 15% ammonia solution	Cathode liquid turns blue, copper deposited on cathode	No changes
2	Anode - cuprammonium cellulose solution	Cathode - 15% ammonia solution	-	Ditto	Cellulose deposited
3	Cathode - cuprammonium cellulose solution	Anode - 15% ammonia solution	-	Copper deposited on cathode	No changes apart from partial displacement of the anode liquid into the cathode space
4	Cathode - 15% ammonia + 1% caustic soda solution	Anode - cuprammonium cellulose solution	-	Cathode liquid turns blue, copper deposited on cathode	Cellulose deposited
5	Cathode - cuprammonium cellulose solution	Anode - 15% ammonia + 1% caustic soda solution	-	Copper deposited	Displacement of anode liquid into cathode space
6	Anode - 15% ammonia + 1% caustic soda solution	Cuprammonium cellulose solution	Cathode - 15% ammonia + 1% caustic soda solution	Liquid turned blue, copper deposited	Part of the anode liquid displaced into central ring
				Cellulose deposited on inner wall of larger porous vessel	

1) Behavior of ammoniacal copper hydroxide solutions on ionites. a) Cation exchange. A known weight of the solution (10, 20, 25, and 50 g) was passed through the cation layer slowly from a buret; the solution flowed out of the column drop by drop; nitrogen, carefully purified to remove oxygen, was first passed through the column to prevent oxidation of ammonia in presence of copper. Copper and ammonia were completely absorbed from the solutions. The absence or presence of copper in the effluent was checked by a drop reaction with benzidine and KBr with the formation of a blue color on the filter paper; the presence of ammonia was detected with phenolphthalein.

To establish the way in which the ionite reacted with the solution, the reversibility or irreversibility of the absorption was determined by washing the column with water and salt solutions (20% solutions of calcium chloride and ammonium nitrate, or 12% hydrochloric acid).

It was shown by prolonged washing of the anionite with water (1500 ml) that irreversible sorption took place in the reaction with ammoniacal copper hydroxide solution, and this was confirmed by quantitative determinations, both when 10 g of 0.5% (copper content) and 10 g of 1% solutions of ammoniacal copper hydroxide solutions were used. Copper was not washed away from the cationite at all, while ammonia was retained in the cationite, despite prolonged washing, in amounts of 22.5 and 23.7 moles (for 0.5 and 1% solutions respectively) per gram-atom of copper.

Washing by electrolytes was used in experiments in which different amounts (10-50 ml) of an ammoniacal solution of copper hydroxide was passed through the cationite layer, the solution being completely absorbed. Various volumes of 20% solutions of calcium and aluminum salts were used to extract the absorbed copper, and the effluent

liquids were analyzed electrolytically for copper (after being made alkaline with ammonia). With a large excess of the salt solutions (400 ml CaCl_2 and 600 ml $\text{Al}(\text{NO}_3)_3$ per 25 g of solution) up to 99.9% of the copper was washed out, which confirms that ion exchange and not mere sorption took place. It is obvious that 1.5 times more calcium chloride than aluminum nitrate was needed to remove the same amount of copper. The copper and ammonia are more conveniently removed by concentrated hydrochloric acid (12%), as large volumes of salt solutions are needed—moreover, when salts were used, the cationites could not be used for further experiments. Without giving tabulated results, we note that 50 ml of hydrochloric acid solution is sufficient to remove up to 99% of the copper.

b) Anion exchange. When the ammoniacal copper solution passed through an anionite column, it flowed through without change of composition, which indicated absence of ion exchange.

2) Ion exchange of cuprammonium cellulose solution. a) **Cation exchange.** The experiments were carried out both in dynamic and static conditions. A 10 g sample of the solution was passed through the cationite, previously freed from air by a stream of nitrogen, in an atmosphere of which the whole experiment was carried out. Lumps of cellulose were deposited on the cationite surface, while copper and ammonia were taken up by the cationite. No copper was found in the effluent liquid. A parallel experiment in static conditions was performed for comparison. The prepared cationite was added to 10 g of cuprammonium cellulose solution in a glass bottle and shaken. The liquid and lumps of cellulose were decanted from the cationite, which was transferred to an adsorption column, where it was washed first with water and then with solutions of the above salts or hydrochloric acid; it was found possible to remove up to 99.6% of the copper which was contained in the solution by these reagents, while water did not wash out copper ions.

These experiments showed that copper and ammonia are absorbed from cuprammonium solution as the result of ion exchange, and not mechanically or by molecular adsorption.

b) Anion exchange. As fine-grained anionites were used (grain size 0.1–0.2 mm) the viscous cuprammonium solution of cellulose could not pass through them, as the use of vacuum or pressure might favor loss of ammonia, and therefore the cation exchange experiment was performed in static conditions. The anionite was added to a known amount of the solution, and the contents were shaken for 1–1.5 hours. The amount of copper, determined electrolytically before and after the anionite treatment, did not change, and the solution was generally unchanged. No ion exchange took place in these conditions, which is contrary to the views of Traube and Hess concerning the presence of copper in the anion of the cellulose cuprammonium complex.

During prolonged interaction of the solution with the M and MMG-1 anionites (during 5–7 days) it was noticed that the solution decomposes with absorption of copper and evolution of cellulose due to insufficient alkalinity of these anionites. With the use of PEK anionite the composition of the solution did not change during prolonged interaction.

3) Ion exchange of cuprammonium solutions of salts and hydroxy-acids. Cation exchange of the following was studied on cationites and anionites: a) cuprammonium solutions of glucose, Rochelle salt, and tartaric acid; b) a mixture of tartaric acid and copper sulfate; and c) ordinary Fehling's solution. In all cases copper was absorbed by the cationite and the solution became colorless.

In experiments with anionites, cuprammonium solutions of glucose, Rochelle salt, and tartaric acid were unchanged. Fehling's solution and the mixture of tartaric acid and copper sulfate were decolorized and copper hydroxide was precipitated as the result of absorption of the sulfate ions and tartaric acid. The experiments were performed in static conditions. The ion exchange medium was added to the solution which was shaken for some time, and the solution was then decanted from the ionite. The color changes which took place in the solutions in presence of cationites were measured by means of a differential electrophotocolorimeter with two photoelectric cells. Uranium glass was used as a light filter. The color of the original solution was compared with the color of the solution decanted from the ionite. For the sake of brevity, tabulated results are not given.

SUMMARY

1. There is no foundation for the view of Traube and Hess that cellulose-cuprammonium compounds are the products of consecutive interaction, with evolution of water and ammonia, between two molecules of cuprammine hydroxide with the glucose residue of the cellulose chain, with the hydroxyl groups of the glucose residues being attached to a copper atom (in the anion) and the cuprammonium residue (in the cation), in linkages of the alcoholate type.

2. By our electrophoretic experiments (with and without separation of the electrode spaces) with ammoniacal

solutions of copper hydroxide and cuprammonium solutions of cellulose and its derivatives, alginic acid, Rochelle salt, sugars, and polyhydric alcohols it was shown that, in contrast to the views of Hess and Messmer, copper is formed only at the cathode. Cupricellulose complexes are not displaced toward the anode either in absence or in presence of caustic soda.

3. The hypothesis of the existence of alcoholate copper in cuprammonium cellulose solutions is also not confirmed by our ion exchange experiments. When ammoniacal copper hydroxide solution, and cuprammonium solutions of cellulose, sugars, and hydroxy acids are passed through cationites, ammonia and copper are quantitatively absorbed in every case, while cellulose is deposited on the cationite. When these solutions are passed through cationites their composition is unchanged, since if copper was present in the anion, copper would be absorbed by the anionite, and the solution would decompose with evolution of cellulose.

4. Cuprammonium cellulose compounds, which do not in reality contain complex anions, should be considered as molecular compounds of variable composition which depends on the equilibrium reactions which take place, and should be likened to alkaline compounds of cellulose (alkali cellulose), which differ from the former only by having a less complicated composition. The solution of polysaccharides in ammoniacal copper hydroxide solutions and in aqueous caustic alkalies has similar features.

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REACTIONS OF DIKETENE

II. REACTIONS OF KETENE WITH INDOLE AND ITS OXYGEN-CONTAINING DERIVATIVES

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Acetoacetyl derivatives of indole and its oxygen-containing derivatives (indoxyl, oxindole, dioxindole, isatin) are not formed by the action of acetoacetic ester on them.

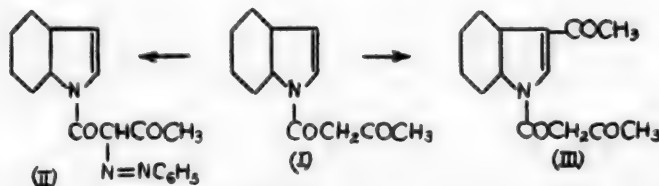
It was therefore of interest to study the reactions of these compounds with diketene in order to obtain a new group of acetoacetic esters — starting materials for the synthesis of various derivatives of the indole series.

The reactive sites in the indole molecule are the secondary amino group and the β -carbon atom, which is activated due to conjugation of the unshared electron pair of the amino groups with the double bond. By analogy with the acetylation of indole [1, 2], its reaction with diketene would be expected to yield N- and C-acetyl derivatives.

Indole in the presence of pyridine [3] formed N-acetoacetylindole (I) by the reaction with diketene. When tertiary amines of different structure but with basicity constants close to that of pyridine were used as catalysts (quinoline, dimethylaniline), the yields of (I) were practically the same; without catalyst the yield of (I) was small, while a highly basic catalyst (triethylamine) directed the reaction toward the formation of dehydroacetic acid, probably as the result of the polymerization rate of diketene being greater than its rate of reaction with indole (see Table 1).

TABLE 1

	Without catalyst	Catalyst			
		Pyridine	Quinoline	Dimethylaniline	Triethylamine
K_b of catalyst	—	$2.4 \cdot 10^{-9}$	$1 \cdot 10^{-9}$	$2.7 \cdot 10^{-10}$	$5.6 \cdot 10^{-4}$
Yield of N-acetoacetylindole (I) (in %)	4.4	43.7	45.0	41.0	—



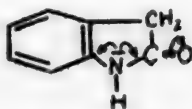
The structure of N-acetylindole (I) was confirmed because: 1) hydrolysis in mild conditions (2% aqueous caustic soda in the cold) resulted in quantitative formation of indole; 2) the azo dye (II) synthesized by coupling (I) with diazobenzene was easily hydrolyzed with the formation of the sodium salt of benzeneazoacetylacetic acid; 3) acylation of (I) by acetic anhydride resulted in the synthesis of N-acetoacetyl-3-acetylindole (III) which was converted by hydrolysis into 3-acetylindole.

If 3-acetoacetylindole had been formed in the given conditions, these reactions could not be carried out.

Indoxyl could form N- and O-derivatives with diketene by reaction with the imino group and transfer of the reaction center to the oxygen atom.

Reaction in benzene solution led to the formation of N-acetoacetylindoxyl (IV) (the O-acyl derivatives are formed by the acylation of indoxyl in an alkaline medium [4, 5] and are hydrolyzed in milder conditions).

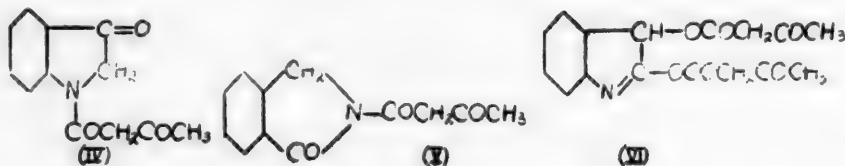
Oxindole, which as a rule reacts in the keto form, did not react with diketene apparently because of reduced basicity of the imino group (conjugation of its unshared electron pair with the carbonyl group).



It was necessary to determine whether the inability of oxindole to react with diketene depends on the simultaneous stabilizing effect of the benzene nucleus and the carbonyl group, or whether the latter plays the decisive role (conjugation with the benzene nucleus alone does not hinder the reaction).

Phthalimidine, in which the imino group is only conjugated with the carbonyl group, gave a quantitative yield of N-acetoacetylphthalimidine (V) with diketene.

In accordance with the above views, dioxindole should not react with diketene. However, it did react, apparently in the dienol form, and yielded a diacetoacetyl derivative. By analogy with the structure of the dibenzene derivative [6] it is probably O,O'-diacetoacetyldehydroxyindole (VI).



Isatin and phthalimide, like dioxindole, did not react with diketene because of their high acidity (k_a of phthalimide is $5 \cdot 10^{-9}$). It was shown earlier that only substances with k_a of 10^{-10} and less react with diketene [7].

The acylating activity of diketene is lower than that of acetic anhydride; the latter forms acetyl derivatives with oxindole, isatin, and phthalimide.

N-Acetoacetylindole (I). To a solution of 4.86 g (0.04 mole) of indole in a mixture of 20 ml of benzene and 20 ml of toluene at 10° , 0.5 ml of pyridine was added, and then 3.36 g (0.04 mole) of diketene* during 1 hour. The mixture was heated for 1 hour on a boiling water bath. The yellow mass obtained after removal of the excess solvent was treated with 1000 ml of 2% caustic soda solution (in 100 ml portions) until the precipitate was practically all dissolved. After neutralization of the alkaline filtrate with 5% hydrochloric acid solution and a stream of carbon dioxide, a pale pink crystalline precipitate was isolated. M.p. 100° (from ethyl alcohol). N-acetoacetylindole is insoluble in water, ethyl alcohol, or ether; it is readily soluble in benzene, acetone, and chlorobenzene. Yield 3.5 g (43.7%).

0.1115 g sub.: 0.2921 g CO_2 ; 0.0560 g H_2O . 0.1451 g sub.: 0.3824 g CO_2 ; 0.0732 g H_2O . 0.1600 g sub.: 9.7 ml N_2 (15° , 767 mm). 0.1241 g sub.: 7.5 ml N_2 (15° , 767 mm). 0.1267 g sub.: 18.02 g benzene: Δt 0.41° . 0.4418 g sub.: 18.02 g benzene: Δt 0.63° . Found %: C 71.50, 71.89; H 5.62, 5.31; N 7.20, 7.18. M 191, 198. $\text{C}_{12}\text{H}_{11}\text{O}_2\text{N}$. Calculated %: C 71.64; H 5.47; N 6.96. M 201.

Hydrolysis of N-acetoacetylindole. 1 g (0.005 mole) of the substance (I) was dissolved in 50 ml of 2% caustic soda solution and left 24 hours. 0.5 g of a substance with m.p. 51° was precipitated. No freezing point depression was produced in a sample mixed with indole. Acetone was detected in the filtrate by the formation of indigo with o-nitrobenzaldehyde.

N-Acetoacetylbenzazindole (II). A solution of 2 g (0.01 mole) of N-acetoacetylindole in 120 ml of ethyl alcohol was mixed with 1 ml of 10% sodium acetate solution. 100 ml (0.01 mole) 0.1 N of diazobenzene was added during 1 hour, with stirring, to the solution cooled to -5° . The solution gradually acquired an intense red color. After 24 hours a yellow precipitate was filtered off and washed with a large volume of alcohol.

The azo dye (II) had m.p. $159-160^\circ$ (from ethyl alcohol); yield 1.29 g (43%).

0.1411 g sub.: 17 ml N_2 (19° , 763 mm). 0.1213 g sub.: 14.4 ml N_2 (19° , 763 mm). Found %: N 14.01, 13.80. $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_3$. Calculated %: N 13.77.

* If the diketene is added without cooling, the yield is rather less, 41%.

Hydrolysis of N-acetoacetylbenzazindole. 0.3 g (0.001 mole) of the azo dye (II) was heated with 20 ml of 5% caustic soda solution for 3 hours on a boiling water bath. During the heating the color of the precipitate changed from bright yellow to orange. The reaction mass was cooled and filtered. M.p. of the precipitate was 195° (from water).

No freezing point depression was found when a sample was mixed with specially synthesized sodium salt of benzeneazoacetylacetic acid [8]. Yield 0.21 g (91%).

N-Acetoacetyl-3-acetylindole (III). 4 g (0.002 mole) of N-acetoacetylindole and 15 ml of freshly distilled acetic anhydride were heated together for 3 hours at 150-170°. The acetic anhydride was distilled off at 10-15 mm. The transparent brown resinous mass was converted into a white crystalline precipitate after treatment with 25 ml of ethyl alcohol followed by trituration.

N-Acetoacetyl-3-acetylindole, m.p. 178-179° (from ethyl alcohol) is difficultly soluble in most organic solvents. Yield 0.55 g (12.5%).

0.1201 g sub.: 0.3029 g CO₂; 0.0558 g H₂O. 0.1324 g sub.: 0.3363 g CO₂; 0.0648 g H₂O. 0.1423 g sub.: 6.6 ml N₂ (16°, 759 mm). 0.1123 g sub.: 5.4 ml N₂ (19°, 756 mm). 0.3126 g sub.: 7.2 g acetone; Δt 0.32°. 0.2132 g sub.: 7.0 g acetone; Δt 0.25°. Found %: C 68.82, 69.31; H 5.19, 5.47; N 5.43, 5.57. M 226, 203. C₁₄H₁₃O₃N. Calculated %: C 69.13; H 5.34; N 5.76. M 243.

Hydrolysis of N-acetoacetyl-3-acetylindole. 0.8 g (0.0032 mole) of the substance (III) was boiled for 1 hour with 10 ml of 5% caustic soda solution. When the solution was cooled, a white flocculent precipitate was formed, which was washed till no alkaline reaction was given.

3-Acetylindole, m.p. 190-191°, sublimed as white leaflets. No freezing point depression was obtained when a sample was mixed with specially prepared 3-acetylindole [2] (m.p. 190-191°).

N-acetoacetylindoxyl (IV). To a suspension of 3.56 g (0.02 mole) of indoxyl acid [9] in 30 ml of benzene, 3 drops of pyridine were added followed by the gradual addition of 3.36 g (0.04 mole) of diketene during 10 minutes. The suspension was then heated 45 minutes on a boiling water bath in a current of hydrogen. After removal of the solvent a brown resin remained, which crystallized on cooling and rubbing. The crystalline mass was treated with 25 ml of ethyl alcohol in the cold, and filtered.

N-Acetoacetylindoxyl, m.p. 110° (from ethyl alcohol), is readily soluble in the cold in acetone, benzene, toluene, and chlorobenzene, and dissolves with difficulty in ether and n-hexane. Yield 0.9 g (37%); when the reaction was carried out without the use of a current of hydrogen, the yield fell to 30%.

0.1196 g sub.: 0.2893 g CO₂; 0.0554 g H₂O. 0.1213 g sub.: 0.2936 g CO₂; 0.0575 g H₂O. 0.1127 g sub.: 6.6 ml N₂ (19°, 775 mm). 0.1273 g sub.: 7.4 ml N₂ (16°, 759 mm). 0.1599 g sub.: 18.46 g benzene; Δt 0.22. 0.2484 g sub.: 18.46 g benzene; Δt 0.32°. Found %: C 66.20, 66.05; H 5.19, 5.31; N 6.74, 6.81. M 206, 214. C₁₂H₁₁O₃N. Calculated %: C 66.36; H 5.06; N 6.45. M 217.

Hydrolysis of N-acetoacetylindoxyl. 0.4 g (0.0018 mole) of the substance (IV) was heated for 3 hours with 10 ml of 5% hydrochloric acid at 80-90°; as the heating progressed, a precipitate of indigo was gradually deposited from the solution. 0.19 g of indigo (81%) was isolated. Acetone was detected in the filtrate made alkaline with 10% caustic soda, by the reaction with o-nitrobenzaldehyde.

N-Acetoacetylphthalimidine (V). A solution of 4 g (0.03 mole) of phthalimidine [10] in 40 ml of toluene was mixed with 0.5 ml of pyridine and 5.5 g (0.06 mole) of diketene, heated for 1 hour at 80-85°, and then boiled 10 minutes. When the brown solution was cooled, 6 g of a copious crystalline precipitate was formed; another 0.6 g was isolated from the filtrate.

N-Acetoacetylphthalimidine, m.p. 135-137° (from toluene) is easily soluble in acetone, ether, benzene, and chlorobenzene. Yield 6.3 g (97%).

0.1234 g sub.: 0.3010 g CO₂; 0.0546 g H₂O. 0.1371 g sub.: 0.3323 g CO₂; 0.0634 g H₂O. 0.1465 g sub.: 8.1 ml N₂ (17.5°, 764 mm). 0.1341 g sub.: 7.4 ml N₂ (16°, 770 mm). 0.1339 g sub.: 21.28 g benzene; Δt 0.16°. 0.2393 g sub.: 21.28 g benzene; Δt 0.28°. Found %: C 65.56, 66.15; H 4.95, 5.18; N 6.49, 6.55. M 208, 204. C₁₂H₁₁O₃N. Calculated %: C 66.35; H 5.07; N 6.45. M 217.

Hydrolysis of N-acetoacetylphthalimidine. A solution of 1 g (0.004 mole) of the substance (V) in 20 g of water was mixed with 0.79 g of soda and boiled for 1 hour. On cooling, 0.6 g of a white crystalline precipitate, m.p. 148-150°, separated out. No freezing point depression was found when a sample was mixed with phthalimidine. Acetone was detected by the o-nitrobenzaldehyde reaction in the alkaline soda filtrate.

2,3-Diacetoacetyldihydroxyindole (VI). 1 g (0.006 mole) of dioxindole [11] was mixed with 30 ml of toluene, 5 drops of pyridine followed by 2 g (0.024 mole) of diketene was added to the suspension. The suspension was heated for 30 minutes with stirring at 50-60°; the dioxindole dissolved.

The brown resin obtained after removal of the solvent, after treatment with 30 ml of cold ethyl alcohol and rubbing, was converted into a white crystalline precipitate of 2,3-diacetoacetyldihydroxyindole; m.p. 170-172° (from ethyl alcohol). The substance is insoluble in most organic solvents. Yield 0.59 g (28%).

0.1481 g sub.: 0.3257 CO₂; 0.0638 g H₂O. 0.1132 g sub.: 0.2510 CO₂; 0.5114 g H₂O. 0.1679 g sub.: 6.3 ml N₂ (19°, 756 mm). 0.1798 g sub.: 7.6 ml N₂ (18°, 757 mm). 0.2046 g sub.: 6.01 g acetone; Δt 0.16°. 0.1600 g sub.: 5.71 g acetone; Δt 0.15°. 0.1521 g sub.: 5.49 g acetone; Δt 0.14°. Found %: C 60.01, 60.51; H 4.95, 5.08; N 4.34, 4.89. M 355, 311, 330. C₁₆H₁₅O₆N. Calculated %: C 60.56; H 4.73; N 5.41. M 317.

SUMMARY

1. Acetoacetyl derivatives of indole and its oxygen-containing derivatives are formed by reaction with diketene in presence of basic catalysts.

2. A relationship has been established between the structure of oxygen-containing indole derivatives and their reactivity toward diketene.

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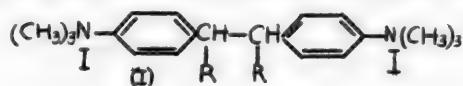
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ALKYLATED DIAMINO DERIVATIVES IN THE DIPHENYLETHANE SERIES

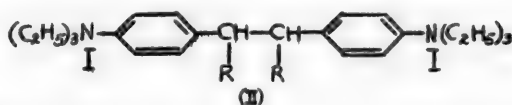
S. F. Torf and N. V. Khromov-Borisov

This paper describes the methods of preparation and the properties of diphenylethane derivatives containing either two tertiary, or two quaternary nitrogen atoms, synthesized by the present authors. Such derivatives containing quaternary nitrogen atoms include compounds with curare-like action[1].

The p,p'-diammonium derivatives were prepared by the interaction of the corresponding p,p'-diamino derivatives of diphenylethane with methyl or ethyl iodide. With the use of methyl iodide six p,p'-diammonium derivatives were obtained, with the general formula (I), where R = H, CH₃, C₂H₅, C₃H₇ and C₄H₉ respectively. With R = CH₃, C₃H₇, C₄H₉ only the meso form was obtained, and with R = C₂H₅, both the meso form and the racemate.



With the use of ethyl iodide two p,p'-diammonium derivatives with the general formula (II) were obtained, where R = CH₃ and C₂H₅ respectively.



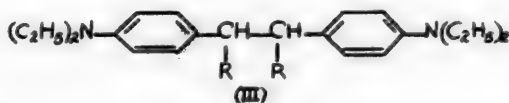
The synthesis of the diamino derivatives used as starting materials was described previously [2].

Good results were not obtained when the methylation and ethylation of diamino derivatives was carried out in the presence of caustic soda. Much better results were obtained when calcium carbonate was used as the substance for binding the acid: the yield was higher and the purification was much simpler.

It was found that the solubility of the above diammonium compounds in water greatly depends on the nature of the radicals at the nitrogen atoms. Diammonium compounds with methyl groups only at the nitrogen atoms are readily soluble in hot water, while the solubility at room temperature is 0.4-1%. Diammonium compounds with ethyl groups only at the nitrogen atoms are practically insoluble even in hot water.

As was to be expected, the ethylation of the original diamino derivatives was much easier if ethyl iodide was used as the alkylating agent; alkylation proceeded less easily when ethyl bromide was used. By making use of this, we were able as desired to carry the reaction as far as quaternary diammonium derivatives by the use of ethyl iodide, or to tertiary diamines by the use of ethyl bromide.

Thus, with the use of ethyl bromide, three derivatives with two tertiary amino groups, with the general formula (III), were obtained, where R = H, CH₃ and C₂H₅ respectively; in the case of the two latter (when R = CH₃, C₂H₅) the meso form was obtained.



EXPERIMENTAL

1,2-Diphenylethane-p,p'-bis-(trimethylammonium) iodide. 1.1 g of p,p'-diamino-1,2-diphenylethane (m.p. 137-139°), 1.2 g of calcium carbonate, 40 ml of methyl alcohol, 20 ml of water, and 4 ml of methyl iodide were heated together for 6 hours under a reflux condenser on a water bath with the alcohol boiling gently. On the next day 10 ml of water was added, the reaction mixture was boiled for 20 minutes with active charcoal and filtered while hot.

TABLE

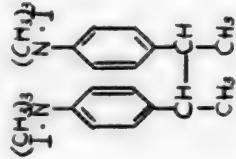
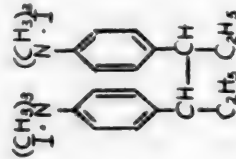
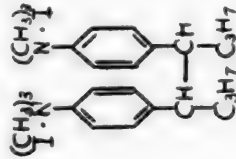
Starting reagents and quantities	Method of purification	Final product Structural formula	m.p., color	Yield (%)	Found %				Calculated %			
					C	H	N	I	C	H	N	I
1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-di-amino-2,3-di-phenylbutane (m.p. 170-172°) 1.2 g CaCO ₃ 1.2 g CH ₃ OH 40 ml, H ₂ O 20 ml, CH ₃ I 4 ml.	Hot filtration. Recrystallization from 40 ml of water		262-265° white	60.4	45.33 45.45	6.09, 6.41	5.04, 5.12	43.80, 43.68	45.52	5.86	4.86	43.79
Meso-p,p'-di-amino-3,4-di-phenylhexane (m.p. 140-142°) 8.8 g CaCO ₃ 7.8 g CH ₃ OH 260 ml, H ₂ O 120 ml, CH ₃ I 26 ml.	Filtration. Recrystallization from 100 ml of water. Distillation of methyl alcohol from the aqueous alcoholic liquor. Recrystallization from 60 ml and then 30 ml of water		226-229° white	78	47.14, 47.25	6.40, 6.52	4.86, 4.86	41.66, 41.84	47.37	6.25	4.60	41.77
Meso-p,p'-di-amino-4,5-di-phenyloctane (m.p. 129-131°) 1 g, CaCO ₃ 0.8 g, CH ₃ OH 27 ml, H ₂ O 14 ml, CH ₃ I 2.7 ml.	Filtration. Recrystallization from 80 ml of water. Recrystallization of undissolved portion of precipitate from the mother liquor		238-241° white	76.7	49.37, 49.17	6.83, 6.84	4.40, 4.59	40.38, 40.08	49.06	6.60	4.40	40.00

TABLE (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-di-amino-5,6-di-phenyldecane (m.p. 105-106°) 1.47 g, CaCO ₃ 1.2 g, CH ₃ OH 40 ml, H ₂ O 20 ml, CH ₃ I 4 ml.	Cooling in freezing mixture before filtration. Recrystallization from 40 ml of water	$\begin{array}{c} (\text{C}_6\text{H}_5)_3\text{I} \cdot \text{N} \cdot \text{I} \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{CH} - \text{CH} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \end{array}$	218-221° white	73.3	50.24, 50.47	7.11, 7.05	4.52, 4.38	38.17, 38.16	50.60	6.93	4.22	38.25
Meso-p,p'-di-amino-2,3-di-phenylbutane (m.p. 170-172°) 1.2 g, CaCO ₃ 1.2 g, C ₂ H ₅ OH 45 ml, H ₂ O 15 ml, C ₂ H ₅ I 4.8 ml.	Filtration. Addition of 2.5 ml of 4% hydrochloric acid to the precipitate suspended in 25 ml of water, till an acid reaction to Congo Red	$\begin{array}{c} (\text{C}_2\text{H}_5)_3\text{I} \cdot \text{N} \cdot \text{I} \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{CH} - \text{CH} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array}$	279-282° cream	52	50.28, 50.48	6.97, 7.10	4.50, 4.43		50.60	6.98	4.22	
Meso-p,p'-di-amino-3,4-di-phenylhexane (m.p. 140-142°) 1.34 g, CaCO ₃ 1.2 g, C ₂ H ₅ OH 42 ml, H ₂ O 18 ml, C ₂ H ₅ I 4.8 ml	Distillation of most of the alcohol under vacuum. Filtration, and treatment of precipitate suspended in water with 4% hydrochloric acid	$\begin{array}{c} (\text{C}_2\text{H}_5)_3\text{I} \cdot \text{N} \cdot \text{I} \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{CH} - \text{CH} \\ \quad \\ \text{C}_6\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	248-250° pale yellow	58	51.84, 51.76	7.51, 7.30	4.42, 4.22		52.02	7.23	4.05	

TABLE (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13
Meso-p,p'-di-amino-1,2-di-phenylethane (m.p. 137-139°) 1.1 g, CaCO ₃ 1.2 g C ₂ H ₅ OH 35 ml, H ₂ O 25 ml, C ₂ H ₅ Br 2.7 ml.	Filtration. Recrystallization from 40 ml of C ₂ H ₅ OH	$(C_2H_5)_2N \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \text{---} \text{CH}_2 \\ \diagdown \diagup \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CH}_2$	83-84° white	36.9	81.24, 81.33	9.96, 10.19	8.79, 8.77		81.48	9.86	8.64	
Meso-p,p'-di-amino-2,3-di-phenylbutane (m.p. 170-172°) 1.2 g, CaCO ₃ 1.2 g, C ₂ H ₅ OH 40 ml, H ₂ O 25 ml, C ₂ H ₅ Br 2.5 ml.	Filtration. Dissolution in 100 ml of hot alcohol and dilution with 37 ml of hot water. Cooling, filtration. Repetition of purification	$(C_2H_5)_2N \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \text{---} \text{CH} \\ \diagdown \diagup \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CH} \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \diagup \end{array} \text{CH}_3$	123-124° white	30.7	81.72, 81.62	10.44, 10.46	8.07, 8.01		81.82	10.33	7.96	
Meso-p,p'-di-amino-3,4-di-phenylhexane (m.p. 140-142°) 1.34 g, CaCO ₃ 1.2 g, C ₂ H ₅ OH 40 ml, H ₂ O 25 ml, C ₂ H ₅ Br 3 ml.	Filtration. Recrystallization from 80 ml of alcohol	$(C_2H_5)_2N \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \text{---} \text{CH} \\ \diagdown \diagup \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CH} \begin{array}{c} \diagup \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \diagup \end{array} \text{CH}_2 \text{C}_2\text{H}_5$	158-159° white	58	81.69, 81.84	10.35, 10.30	7.06, 7.04		82.10	10.50	7.37	

The mixture was cooled and the precipitate formed was filtered off. The weight of the air-dry substance was 2.6 g, m.p. 227-232°. Recrystallization from 30 ml of water with active charcoal yielded 2.17 g of 1,2-diphenyl-ethane-p,p'-bis-(trimethylammonium) iodide, white in color, m.p. 229-232°. Yield 77.5%.

0.1380, 0.1282 g sub.: 0.2204, 0.2034 g CO₂; 0.0652, 0.0638 g H₂O. 0.1583, 0.1526 g sub.: 5.8, 5.6 ml 0.1 N. H₂SO₄. Found %: C 43.55, 43.26; H 5.29, 5.56; N 5.13, 5.14. C₂₆H₃₀N₂I₂. Calculated %: C 43.47; H 5.43; N 5.07.

The other diammonium quaternary derivatives, and also the derivatives with tertiary amino groups, were obtained by a method as described above, with some modifications in the methods of isolation and purification of the reaction products. The results of these experiments are shown in the following table.

A description is also given of the preparation of the preparation of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide racemate, in view of the considerable difference in the method of isolation and purification.

The racemate of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide. 0.67 g of the racemate of p,p'-diamino-3,4-diphenylhexane (m.p. 70-71°), 0.6 g of calcium carbonate, 20 ml of methyl alcohol, 10 ml of water, and 10 ml of methyl iodide were heated together on the water bath for 5 hours with gentle boiling. On the next day the reaction mixture was filtered to remove a slight precipitate of calcium carbonate and distilled under a vacuum (with the water bath temperature kept not above 60°) to drive off methyl alcohol and water.

15 ml of redistilled acetone was added to the oily residue, and the solution formed was diluted with anesthetic grade ether. The lower layer which separated out was poured into 15 ml of acetone. The solution was left overnight in freezing mixture. The precipitate was filtered off, washed with acetone mixture and dried in a vacuum desiccator. The weight of the precipitate was 1.08 g. The powdered precipitate was thoroughly triturated with 10 ml acetone and filtered off after 2 hours. The yield was 0.8 g of the racemate of 3,4-diphenylhexane-p,p'-bis-(trimethylammonium) iodide, white in color. M.p. 194-196°. Yield 52.6%.

0.2927, 0.2228 g sub.: 10.75 ml (21°, 731.4 mm), 8.5 ml (21°, 736 mm) N₂. Found %: N 4.10, 4.30. C₂₄H₂₈N₂I₂. Calculated %: N 4.60.

SUMMARY

1. The alkylation of p,p'-diamino derivatives of 1,2-diphenylethane, meso-2,3-diphenylbutane, 3,4-diphenylhexane (meso and racemate), meso-4,5-diphenyloctane, and meso-5,6-diphenyldecane was studied; a number of new derivatives was produced, both with two quaternary ammonium groups and with two tertiary amino groups.

2. The use of calcium carbonate as the reagent for binding hydrogen iodide favors an increased yield and facilitates the purification of the ammonium derivatives obtained.

3. It was found that when ethyl bromide reacts with p,p'-diamino derivatives, primary amino groups are converted into tertiary amino groups, while when ethyl iodide acts in the same conditions, quaternary ammonium groups are formed.

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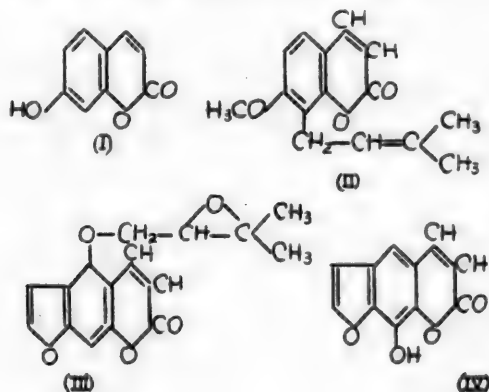
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ULTRAVIOLET SPECTRA OF SOME NATURAL COUMARINS

G. V. Pigulevsky and G. A. Kuznetsova

The absorption spectra of natural coumarins, which also include the furocoumarins, have been studied little at the present time. The only information available is on bergaptol [1]; we therefore made a study of compounds belonging to the hydroxy- and methoxycoumarins (umbelliferone, osthole) and also more complex compounds with a furan ring in the molecule (furocoumarins); hydroxypeucedanin, xanthotoxol.



These compounds are found in the resins of the roots of plants belonging to the Umbelliferae. In particular, osthole, hydroxypeucedanin, and xanthotoxol were found [3, 4] in the roots of *Frangos pabularia* Lindley, which grow in mountainous and submountainous regions of the Central Asian republics of the USSR. Their simultaneous occurrence in the same plant is rather reminiscent of a similar phenomenon for another class of compounds — the terpenes. Essential oils consisting of terpenes are often found to contain terpenes of closely related structure. A knowledge of the absorption spectra of coumarin derivatives may help in the study of such compounds found in plants. The absorption spectra were studied with the aid of the Q-12 quartz spectrograph. A hydrogen lamp was used as the source of the continuous radiation spectrum. The absorption spectrum of each compound was obtained by two methods; 1) the variable thickness method, which gave a clear qualitative and semiquantitative picture of the molecular absorption spectra, and 2) Henri's method, by which visual photometric measurements could be carried out and the molecular absorption spectra determined. The values obtained were used to plot the molecular absorption curves. The molecular absorption coefficient K was calculated from the Lambert-Beer Formula:

$$K = \frac{\log I / I_0}{cd}$$

where c is the molecular concentration and d is the thickness of the layer.

Absorption spectrum of umbelliferone (hydroxycoumarin) (I). The umbelliferone had m.p. 223-224°. The absorption spectrum was taken in C_2H_5OH solution (0.0251 moles/liter). The absorption curve for umbelliferone (Fig. 1, Curve 1) shows that the absorption region lies in the wave length range 3500-2300 Å.

Umbelliferone has one broad band with an absorption maximum at λ 3205 Å and one small band with an absorption maximum at λ 2520 Å. In comparison with the absorption spectrum of benzene [2] there is a strong shift toward the longer wave lengths, due to structural peculiarities of hydroxycoumarin.

Absorption spectrum of osthole (II). Osthole, isolated from *Frangos pabularia* resin, with m.p. 84°, was used. The absorption spectrum of osthole was taken in C_2H_5OH solution (0.0241 moles/liter). Figure 1 shows the absorption curve for osthole (Curve 2). The absorption region for osthole lies in the wave length region 3500-2300 Å.

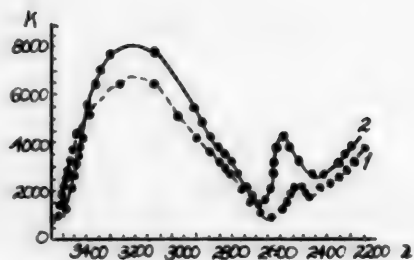


Fig. 1. Absorption curves for umbelliferone (1) and osthole (2).

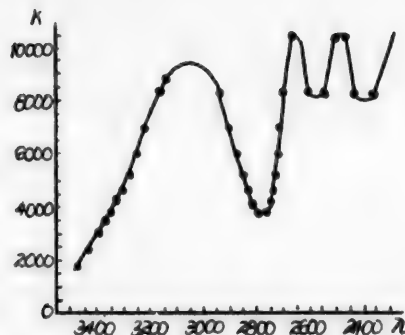


Fig. 2. Absorption curve for hydroxyypeucedanin.

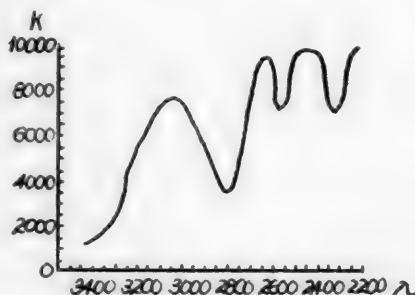


Fig. 3. Absorption curve for xanthotoxol.

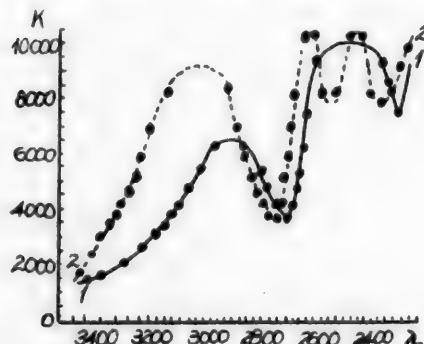


Fig. 4. Absorption curves for substance of m.p. 174-175° (1) and hydroxyypeucedanin (2).

The osthole spectrum consists of one broad absorption band with an absorption maximum at λ 3220 Å and an absorption band at λ 2585 Å. The great resemblance between the spectra of osthole and umbelliferone is explained by the close similarity of their structures.

Absorption spectrum of hydroxyypeucedanin (III). Hydroxyypeucedanin, like osthole, was isolated from *Prangos pabularia* resin. M. p. 142-142.5°. The absorption spectrum was taken in C_2H_5OH solution (0.0228 moles/liter). Hydroxyypeucedanin (furocoumarin) differs from osthole and umbelliferone by the presence of a furan ring. Absorption in the 2800-2100 Å region is characteristic for the latter. The absorption curve for hydroxyypeucedanin (Fig. 2) shows that its spectrum, in contrast to the spectra of umbelliferone and osthole, consists of three absorption bands in the wavelength range 3500-2200 Å. The maxima of the absorption bands are at λ 3060, 2660 and 2495 Å. A comparison of the absorption bands of hydroxyypeucedanin and osthole shows a difference in their nature, although they both lie in the same wave length region. There is no doubt that structural differences (between coumarin and furocoumarin) determine the features of their absorption spectra.

Absorption spectrum of xanthotoxol (IV). Xanthotoxol was isolated from *Prangos pabularia* resin. M.p. 243-245° (decomp.). The absorption spectrum was taken in C_2H_5OH solution (0.024 mole/liter). Analysis of the absorption curve of xanthotoxol (Fig. 3) shows that its spectrum consists of three absorption bands in the region 3500-2000 Å. The absorption maxima are at λ 3055, 2650 and 2470 Å.

The absorption spectrum of the furocoumarin prangenin, described previously [4], is very close to the spectrum of hydroxyypeucedanin.

Comparison of the absorption spectra of the three furocoumarins shows great similarity between them: the absorption bands (see table) of all three substances lie in the same spectral region; the bands have very similar contours, that is, a similar distribution of the absorption intensities in the absorption bands. They are also very similar to the absorption spectrum of bergaptol, described in the literature.

Furocoumarins	Absorption band maxima (Å)			Furocoumarins	Absorption band maxima (Å)		
Prangenin	3000	2670	2470	Hydroxyypeucedanin	3060	2660	2495
Xanthotoxol	3055	2650	2470	Bergaptol	3070	2675	2500

Absorption spectrum of the substance with the composition $C_{15}H_{15}O_4COOH$. The substance of unknown structure was isolated together with the other products from *Prangos pabularia* resin. Its m.p. was 174-175°. The absorption spectrum was taken in C_2H_5OH solution (0.0251 moles/liter). Fig. 4 shows the absorption curves for the substance with m.p. 174-175° (Curve 1) and hydroxypeucedanin (Curve 2). A comparison of the absorption curves for the two substances reveals some similar features. The absorption bands lie in the same wave length region and have some similarity of outline. There is a difference in the distribution of absorption intensities in the band which lies in the shorter wave region. For example, the maxima of the absorption bands for the substance with m.p. 174-175° lie at λ 2950, 2515 Å, and for hydroxypeucedanin at 3060, 2660 and 2495 Å. A certain similarity between the spectra of these substances suggests the presence of some common structural elements. The wave length shift in the spectrum of the substance of m.p. 174-175° relative to the spectrum of hydroxypeucedanin may be attributed to the presence of a carboxyl group in the molecule and different positions of the substituents. In addition, according to the formula $C_{16}H_{16}O_6$ ascribed to the substance, it is more saturated than hydroxypeucedanin, $C_{16}H_{14}O_5$, which fully explains the shift of the absorption band into the region of shorter waves.

We express our gratitude to S. N. Andreev for his assistance in the work.

SUMMARY

The spectra of some natural coumarins (umbelliferone, osthole, hydroxypeucedanin, and xanthotoxol) have been obtained for the first time. The absorption spectra of furocoumarins differ sharply from the absorption spectra of hydroxy- and methoxycoumarins. The possibility of using ultraviolet spectroscopy for solving problems of the structure of new compounds of the coumarin series is pointed out.

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* T. p. = C. B. Translation pagination.

REACTIONS OF SYMMETRICAL AROMATIC COMPOUNDS OF MERCURY WITH PHENOLS

I. STUDY OF THE THERMAL STABILITY OF COMPOUNDS OF THE GENERAL FORMULA $(RC_6H_4)_2Hg$

M. M. Koton and V. F. Martynova

One of the present authors [1] earlier developed a method for the mercurization of phenols with the aid of symmetrical aromatic compounds of mercury of the general formula Ar_2Hg . In continuation of this, we studied the reaction between phenols and substituted aromatic bis-compounds of mercury with the general formula $(RC_6H_4)_2Hg$, where $R = NH_2, OH, CH_3, NO_2, COOH$, in order to investigate the influence of the nature of the substituents on the rate and character of the reaction with different phenols.

The reaction of mercurization by symmetrical mercury compounds proceeds under the influence of heat, and therefore it might be expected, on the basis of the radical mechanism of this reaction, that the ease with which the mercurization reaction proceeds would depend on the thermal stability of the symmetrical mercury compounds; we therefore commenced our research with a study of the thermal stability of symmetrical substituted mercuroorganic compounds of the general formula $(RC_6H_4)_2Hg$. The experiments were carried out at 130-150° for 3 hours, after which the quantity of free metallic mercury evolved was determined.

Our investigations showed that the $(RC_6H_4)_2Hg$ compounds differ in their thermal stability. Mercuroorganic compounds containing substituents of the second type ($NO_2, COOH$) in the benzene ring were found to be thermally stable, and metallic mercury was not evolved even during heating to 150°.

The mercuroorganic compounds containing substituents of the first type (NH_2, OH, CH_3), on the contrary, already decomposed at 130° with the evolution of metallic mercury, the amount of mercury formed depending on the nature of the substituent in the benzene ring (Table 1).

TABLE 1

Thermal Stability of $(RC_6H_4)_2Hg$ Compounds. Weight taken, 0.2 g; duration of experiment 3 hours

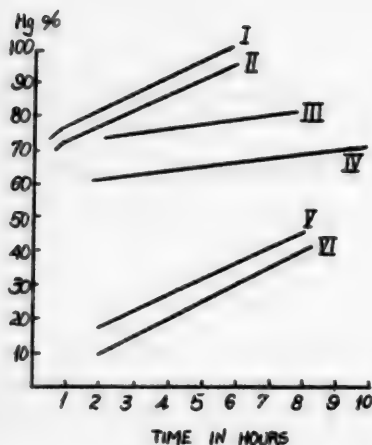
Formula $(RC_6H_4)_2Hg$	Temperature	Amount of metallic mercury formed (in %)	Content of Hg in residue (in %)	
			Found	Calculated
$(p-H_2NC_6H_4)_2Hg$	130°	23.85	52.09	51.94
$(o-HOC_6H_4)_2Hg$	130	20.69	51.77	51.53
$(p-CH_3OC_6H_4)_2Hg$	130	5.05	47.90	48.30
$(m-NO_2C_6H_4)_2Hg$	150	None	45.20	45.04
$(o-NO_2C_6H_4)_2Hg$	150	None	44.97	45.04
$(p-HOOC_6H_4)_2Hg$	150	None	44.97	44.82

The compounds may be placed in the following series according to their rates of decomposition:



It only proved possible to draw conclusions concerning the stability of the bonds between mercury and the organic radicals, on the basis of thermal stability studies, for compounds containing substituents of the first type. This was not possible for mercuroorganic compounds containing substituents of the second type in view of their complete thermal stability in such conditions.

It was previously shown [2] that symmetrical aromatic compounds of mercury readily decompose on heating in presence of phenols; the following series was obtained for the decomposition rates of compounds of the formula R_2Hg : $C_6H_5CH_2 > C_6H_5 > C_{10}H_7$.



Decomposition of $(RC_6H_4)_2Hg$ in presence of pyrogallol at 130°.

I) $(p-H_2NC_6H_4)_2Hg$, II) $(o-HOC_6H_4)_2Hg$,
 III) $(p-CH_3OC_6H_4)_2Hg$, IV) $(m-O_2NC_6H_4)_2Hg$,
 V) $(o-O_2NC_6H_4)_2Hg$, VI) $(p-HOCC_6H_4)_2Hg$.

TABLE 2

Thermal Stability of $(RC_6H_4)_2Hg$ Compounds in Presence of Pyrogallol at 130°. Weight taken 0.15 g

Starting substance	Time (hours)	Amount of metallic mercury formed		Starting substance	Time (hours)	Amount of metallic mercury formed	
		(in g)	(in %)			(in g)	(in %)
$(p-NH_2C_6H_4)_2Hg$	0.5	0.0593	74.55	$(p-CH_3OC_6H_4)_2Hg$	7	0.0604	83.35
	1	0.0624	78.15		2	0.0439	62.64
	2	0.0644	82.20		4	0.0455	65.94
	3	0.0680	86.85		6	0.0471	68.21
	4	0.0731	92.15	$(m-NO_2C_6H_4)_2Hg$	8	0.0486	70.20
	5	0.0758	96.80		10	0.0497	71.69
$(o-HOC_6H_4)_2Hg$	6	0.0775	99.82		2	0.0130	19.22
	0.5	0.0505	70.50		4	0.0183	27.03
	1	0.0529	73.95	$(o-NO_2C_6H_4)_2Hg$	6	0.0250	37.07
	2	0.0566	78.00		8	0.0319	47.25
	3	0.0600	83.85		2	0.0079	11.55
	4	0.0624	87.01	$(p-HOCC_6H_4)_2Hg$	4	0.0133	21.63
$(p-CH_3OC_6H_4)_2Hg$	6	0.0690	96.50		6	0.0228	31.99
	2	0.0548	75.45		8	0.0289	42.64
	4	0.0568	78.15				
	6	0.0595	81.80				

Thermal stability of $(RC_6H_4)_2Hg$ compounds in presence of p-aminophenol and hydroquinone

The thermal stability of $(RC_6H_4)_2Hg$ was studied not only in the presence of pyrogallol, but also in the presence of p-aminophenol and hydroquinone. The results of these experiments were in full qualitative agreement with the results for thermal decomposition, and the difference was purely quantitative. When pyrogallol was replaced by p-aminophenol and hydroquinone, the stability of the $(RC_6H_4)_2Hg$ compounds increased (less mercury was evolved at the same temperature and in the same heating time) (Table 3).

It was therefore decided to use this method to determine the stability of the bond between the mercury atom and the benzene ring containing substituents of the second type. For comparison, these experiments were also performed with mercurioorganic compounds containing substituents of the first type.

The results of the experiments showed that in presence of pyrogallol at 130° the thermal stability of all the $(RC_6H_4)_2Hg$ compounds studied falls sharply, as was shown by the amounts of mercury evolved, which were considerably greater than during ordinary thermal decomposition in absence of pyrogallol (Table 2). In such conditions mercurioorganic compounds with substituents of the second type were also thermally unstable. Their thermal stabilities also differed, and depended not only on the nature of the substituent, but on its position in the benzene ring. Their rates of decomposition form the following series:



All the $(RC_6H_4)_2Hg$ compounds studied form the following series according to their decomposition rates in presence of pyrogallol (see figure):

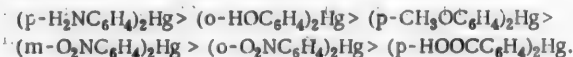


TABLE 3

Comparative Stability of $(RC_6H_4)_2Hg$ in Presence of Additions. Weight taken 0.2 g; duration of experiment 3 hours

Formula of $(RC_6H_4)_2$	Temperature	Evolution of metallic mercury (in %)		
		Pyrogallol	p-Aminophenol	Hydroquinone
$(p-H_2NC_6H_4)_2Hg$	130°	86.85	74.50	72.38
$(p-CH_3OC_6H_4)_2Hg$	130	76.43	58.26	52.20
$(m-O_2NC_6H_4)_2Hg$	150	58.70	10.75	9.50
$(o-O_2NC_6H_4)_2Hg$	150	30.70	8.79	8.21

EXPERIMENTAL

In all the experiments the substances or mixtures were heated in sealed glass ampoules in an oil thermostat with strict temperature control. In the experiments with pyrogallol, hydroquinone, and p-aminophenol, the contents of the ampoules consisted of a black caked mass containing metallic mercury. The precipitate was treated with an alcoholic solution of 0.5 N caustic potash to remove phenolic oxidation products. The determination of metallic mercury and the analysis for mercury content were carried out by the usual methods.

SUMMARY

1. Substituted diaryl mercury derivatives of the $(RC_6H_4)_2Hg$ type fall into two groups according to their thermal stability — the first, containing substituents of the first type (OH, NH_2 , CH_3O), and the second, containing substituents of the second type (NO_2 , COOH).

The compounds of the first group are less stable thermally than the compounds of the second group.

2. It is shown that the thermal stability of $(RC_6H_4)_2Hg$ compounds decreases sharply in presence of pyrogallol, p-aminophenol, and hydroquinone, and mercurioorganic compounds with substituents of the second type become unstable in these conditions.

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INVESTIGATION OF THE ACTION OF ALUMINUM CHLORIDE IN A STREAM OF HYDROGEN CHLORIDE GAS ON SOME NAPHTHALENE TETRABROMIDES

Z. I. Stetsura

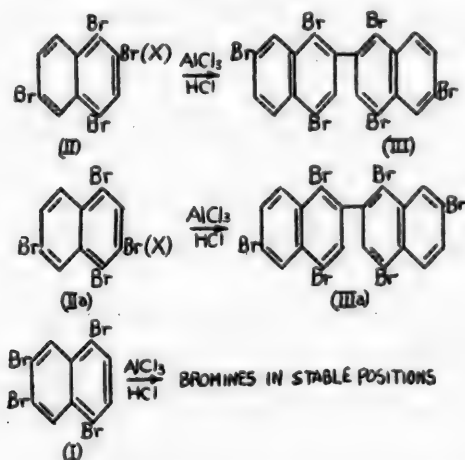
The mobility of the bromine atom in the naphthalene molecule, resulting in its migration from one position to another, has been repeatedly reported in the literature. Roux [1] showed as early as 1887 that α -bromonaphthalene was converted into the β -isomer by gentle heating in carbon disulfide solution in presence of AlCl_3 . Zalkind and Filinov [2] heated a solution of α -bromonaphthalene in carbon disulfide in presence of AlCl_3 and hydrogen chloride, and obtained the β -isomer. Lohfert [3] reported that by the action of AlCl_3 in a stream of hydrogen chloride on 1,2-dibromonaphthalene, m.p. 68° , he was able to cause bromine to migrate, in various experiments, from the 1,2 positions to the 1,4, or 1,5, or 2,6 positions.

Lohfert's error was that he incorrectly took the original dibromide to be 1,2-dibromonaphthalene. Actually his dibromide was a mixture of 1,4- and 1,5-dibromonaphthalenes. Lohfert was evidently not aware of the work of Zalkind and Faerman [5], who showed convincingly that direct bromination of naphthalene gives a mixture of 1,4- and 1,5-dibromonaphthalenes, and not the 1,2 isomer. We studied the action of AlCl_3 in a current of hydrogen chloride on 1,4-dibromonaphthalene and, in other experiments, on 1,5-dibromonaphthalene, and found that in both cases the bromine atoms migrate to form 2,6-dibromonaphthalene [4].

It was interesting to note the effect of an increase in the number of bromine atoms on their mobility in the naphthalene molecule. We studied 1,4,6,7- (I) and 1,X,4,6-tetrabromonaphthalenes. As was established by Zalkind and Stetsura [6], the latter may have the structure of the 1,2,4,6- (II) or of the 1,3,4,6-isomer (IIa).

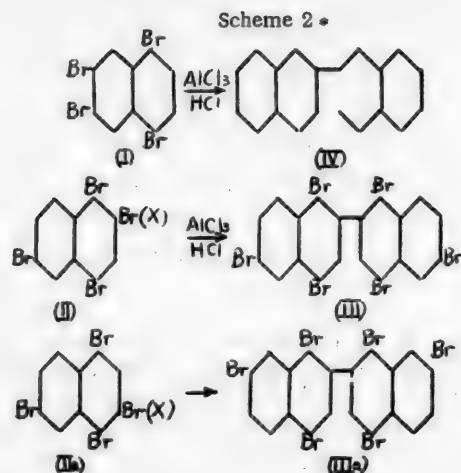
Experiments were at first carried out with AlCl_3 which was synthesized in the laboratory and sublimed into the reaction vessel. In these conditions the tetrabromides behaved differently. Thus, the tetrabromonaphthalene (I) proved more stable and was isolated unchanged, while the tetrabromonaphthalene in which three bromine atoms are in one ring (II or IIa) condenses to form hexabromonaphthalene,*to which the structure (III or IIIa) may be ascribed (see Scheme 1).

Scheme 1



Quite different results were obtained when the AlCl_3 used for the reaction was not sublimed into the reaction vessel, but was in the form of the preparation obtained by Radsianowski's method [7], containing an admixture of metallic aluminum. In this case the tetrabromonaphthalene (I) was strongly resinified and a small amount of dinaphthyl (IV) was isolated, while the reaction with the tetrabromonaphthalene (II or IIa) gave hexabromodinaphthyl (III or IIIa) and dinaphthyl (IV) (see Scheme 2).

* The following seems to be an error in the original text: "hexabromodinaphthyl" is undoubtedly what is meant here; the schemes do not seem to agree with the text, and Scheme 2 omits the double bonds. — Publisher.



The substitution of bromine atoms by hydrogen in the formation of dinaphthyl apparently took place as the result of a reaction between hydrogen chloride and aluminum. The mechanism of the reaction for the formation of dinaphthyl is as follows: the first step is the condensation of naphthalene tetrabromides to form hexabromodiphenyl because of the great mobility of bromine in the β -position, then, in presence of active hydrogen, bromine atoms are substituted to form dinaphthyl, while in absence of active hydrogen only hexabromodiphenyl with m.p. 232° is formed. An increase in the number of bromine atoms in the naphthalene molecule hinders migration and sets up conditions for the reaction to take a new direction. The condensation of naphthalene rings which was observed in our experiments is shown in Schemes 1 and 2.

EXPERIMENTAL

Action of AlCl_3 in a stream of hydrogen chloride on 1,2,4,6- (II) or 1,3,4,6- (IIa) tetrabromonaphthalene with m.p. 119-120°. Aluminum chloride was prepared by heating aluminum in the form of granules in a stream of dry hydrogen chloride gas in an electric furnace. The required amount of the prepared AlCl_3 was driven off from a retort into the reaction vessel, covered with carbon disulfide, a stream of hydrogen chloride was passed, and a concentrated solution of tetrabromonaphthalene in carbon disulfide was added drop by drop. The reaction mixture was warmed by an electric lamp. The hydrogen chloride gas was passed for 5 hours. The original tetrabromonaphthalene and hexabromodiphenyl, m.p. 232°, were isolated from the strongly resinified mixture.

0.1112 g sub.; 8.15 ml AgNO_3 [T (by bromine) 0.0088] (Pringsheim). 0.132 g sub.; 21 g benzene: Δt 0.045°. 0.0322 g sub.; 0.6044 g camphor: Δt 2.9° (Rost). Found %: Br 64.50. M 699, 736.65. $\text{C}_{20}\text{H}_8\text{Br}_6$. Calculated %: Br 65.96. M 728.

Action of AlCl_3 in a stream of hydrogen chloride on 1,4,6,7-tetrabromonaphthalene with m.p. 170-171°. The reaction was carried out in the conditions described above, but the amounts of catalyst were varied. In some experiments 1 mole of catalyst was taken per 1 mole of the tetrabromide, while in other experiments the amount of catalyst was two or three times as much. No visible changes were observed in the reaction mixture during the experiments. Some resin formed on the catalyst grains on heating. Treatment of the products resulted in the original 1,4,6,7-tetrabromonaphthalene being obtained back unchanged.

Action of AlCl_3 prepared by Radsiwanski's method, in a stream of hydrogen chloride on 1,X,4,6-tetrabromonaphthalene with m.p. 119-120° (II or IIa). A small amount of carbon disulfide was poured over 5 g of aluminum grains, and a stream of dry hydrogen chloride was passed for 12 hours. The aluminum granules became coated with a crust of AlCl_3 . Small portions of a solution of 1,X,4,6-tetrabromonaphthalene (II or IIa) in carbon disulfide were then added. The mixture was warmed by an electric lamp. Evolution of small bubbles of gas, and strong resinification, were observed during the reaction. After repeated recrystallization of the reaction products, two substances were isolated, with m.p. 232 and 185°. The substance of lower melting point was obtained in the form of plates with bluish-pink fluorescence after several recrystallizations from alcohol and acetic acid. This substance did not contain bromine.

* AlCl_3 was prepared by Radsiwanski's method [7].

0.0766 g sub.; 30.68 g benzene; Δt 0.05°. Found: M 250. $C_{20}H_{14}$. Calculated: M 254.

Analysis of the substance with m.p. 232°.

0.1449 g sub.; 10.5 ml $AgNO_3$ [T (by bromine) 0.0088] (Pringsheim). 0.0548 g sub.; 23.9 g benzene; Δt 0.016°. Found %: Br 63.77. M 718.7. $C_{20}H_8Br_8$. Calculated %: Br 65.96. M 728.

No depression of freezing point was produced when a specimen was mixed with the hexabromodinaphthyl obtained previously.

Action of $AlCl_3$ prepared by Radsiwanski's method, in a stream of hydrogen chloride on 1,4,6,7-dibromonaphthalene with m.p. 171°. 10 g of 1,4,6,7-tetrabromonaphthalene dissolved in carbon disulfide was added to aluminum chloride prepared by Radsiwanski's method. Hydrogen chloride was passed for 8 hours. After treatment of the strongly resinified reaction products, a small amount of dinaphthyl with m.p. 185° was isolated. No depression of melting point was obtained when a specimen was mixed with the dinaphthyl prepared previously.

The subject of the present study was proposed by the late Prof. Yu. S. Zalkind.

SUMMARY

1. The mobility of bromine atoms decreases with their increased numbers in the naphthalene molecule.
2. 1,X,4,6-, 1,2,4,6- or 1,3,4,6- tetrabromonaphthalenes give a reaction in which condensation of the naphthalene nuclei takes place, in the same conditions in which bromine migrates from the alpha to the beta position in dibromides.
3. In presence of nascent hydrogen, the condensation of the naphthalene nuclei is preceded by substitution of the bromine atoms by hydrogen.
4. A tetrabromide in which there are three bromine atoms in one ring is more active than a tetrabromide with two bromine atoms in each ring of the naphthalene molecule.

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POLAROGRAPHIC STUDY OF THE HYDROGENATION PROCESS

VI. HYDROGENATION OF MIXTURES OF MESITYL OXIDE WITH DISUBSTITUTED ETHYLENES

A. L. Markman

Skita [1] and Adams [2] have studied the hydrogenation of mesityl oxide, which is a representative of the tri-substituted ethylene group. The behavior of mesityl oxide during hydrogenation of its binary mixtures with disubstituted ethylene derivatives was investigated by S. V. Lebedev [3]. He found that in such mixtures the disubstituted ethylene is hydrogenated first, and mesityl oxide begins to be hydrogenated only after the former is fully saturated.

The polarographic behavior of mesityl oxide [4] was used to study the hydrogenation of some of its binary mixtures with disubstituted ethylene derivatives by the method described previously [5].

EXPERIMENTAL

1. Hydrogenation of a mixture of mesityl oxide with maleic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml of 0.1 N HCl in 50% ethanol for the polarographic analysis. In these conditions mesityl oxide gives no polarographic record, while maleic acid gives a distinct wave (Table 1, Fig. 1). The selectivity index in this case had the value $S = 0.988$ [6]. In a parallel experiment, $S = 0.977$.

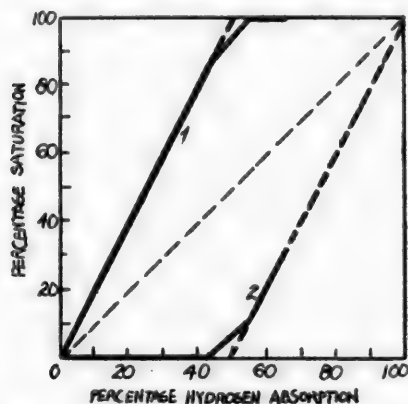


Fig. 1. Hydrogenation of a mixture of mesityl oxide with maleic acid (catalyst - palladium).

1) Maleic acid, 2) mesityl oxide.

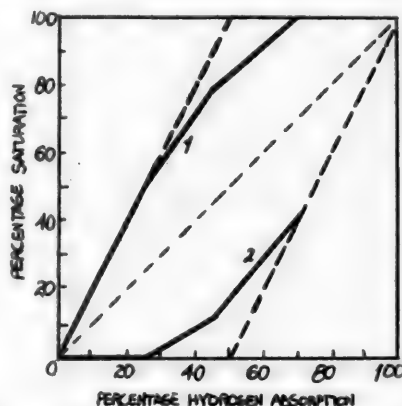


Fig. 2. Hydrogenation of a mixture of mesityl oxide with maleic acid (catalyst - platinum).

1) Maleic acid, 2) mesityl oxide.

TABLE 1

Hydrogenation of a Mixture of Mesityl Oxide with Maleic Acid in the Presence of Pd. 0.58 g of maleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 30 ml of alcohol and 10 ml of water. Bath temperature 40°, air temperature 16°, Pressure 726 mm. Theoretical absorption of hydrogen H_2 248.2 ml. π $1/2 - 0.73$ V

H ₂ absorption		Wave height (mm)	Maleic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5} \cdot$	$\Delta C \cdot 10^{-5} \cdot$	Saturation(%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation(%)
0	0	440	250	0	0	250	0	0
25.8	10.4	350	198	52	20.8	250	0	0
52.2	21.0	255	145	105	42.0	250	0	0
79.4	32.0	160	90	160	64.0	250	0	0
108.3	43.6	56	32	218	87.2	250	0	0
136.9	55.2	0	0	250	100	225	25	10.0
160.9	64.8	0	0	250	100	176	74	29.6

• In this and the other tables C is the concentration, and ΔC is the fall in concentration of each of the components. Both values are in moles/liter.

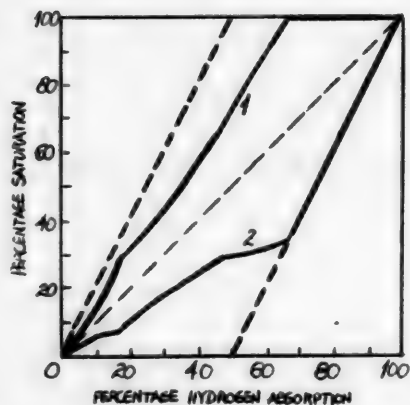


Fig. 3. Hydrogenation of a mixture of mesityl oxide with fumaric acid (catalyst - palladium).
1) Fumaric acid, 2) mesityl oxide.

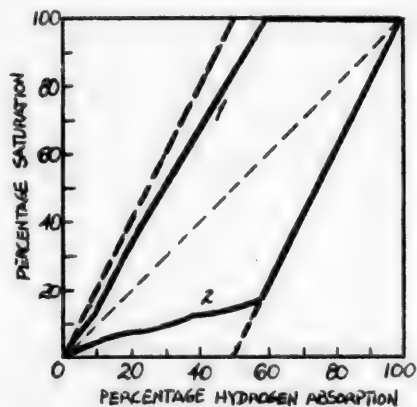


Fig. 4. Hydrogenation of a mixture of mesityl oxide with cinnamic acid (catalyst - palladium).
1) Cinnamic acid, 2) mesityl oxide.

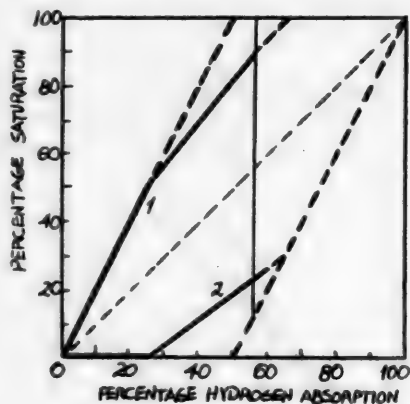


Fig. 5. Hydrogenation of a mixture of mesityl oxide with oleic acid (catalyst - palladium).
1) Mesityl oxide, 2) oleic acid.

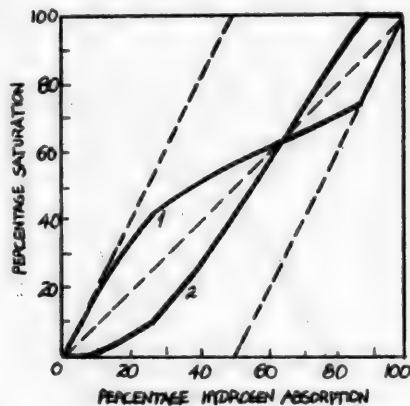


Fig. 6. Hydrogenation of a mixture of mesityl oxide with oleic acid (catalyst - platinum).
1) Mesityl oxide, 2) oleic acid.

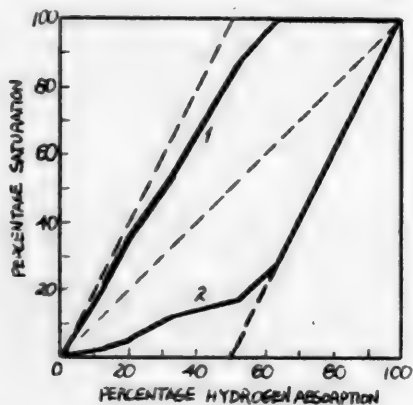


Fig. 7. Hydrogenation of a mixture of mesityl oxide with itaconic acid (catalyst - palladium).
1) Mesityl oxide, 2) itaconic acid.

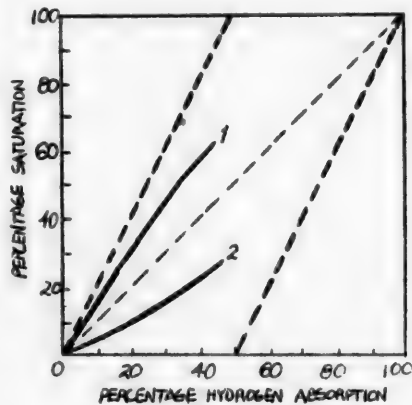


Fig. 8. Hydrogenation of a mixture of mesityl oxide with itaconic acid (catalyst - platinum).
1) Itaconic acid, 2) mesityl oxide.

TABLE 2

Hydrogenation of a Mixture of Mesityl Oxide with Maleic Acid in the Presence of Pt
0.58 g of maleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 40°, air 23°. Pressure 720 mm. Theoretical absorption of hydrogen H_2 256.4 ml

H ₂ absorption		Wave height (mm)	Maleic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	775	250	0	0	250	0	0
21.0	8.2	650	209	41	16.4	250	0	0
43.3	16.9	515	166	84	33.6	250	0	0
66.8	26.1	372	120	130	52.0	250	0	0
116.8	45.6	160	52	198	79.2	220	30	12.0
143.5	56.0	92	30	220	88.0	190	60	24.0
172.1	67.1	20	5	244	97.6	158	92	36.8

TABLE 3

Hydrogenation of a Mixture of Mesityl Oxide with Fumaric Acid in the Presence of Pd
0.58 g of fumaric acid, 0.49 g of mesityl oxide, 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 18°. Pressure 720 mm. Theoretical absorption of hydrogen H_2 254 ml $\pi_{1/2} = 0.82$ V

H ₂ absorption		Wave height (mm)	Fumaric acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	240	250	0	0	250	0	0
21.1	8.4	212.5	221	29	11.6	237	13	5.2
43.3	17.2	176	183	67	26.8	231	19	7.6
66.8	26.5	148	154	96	38.4	214	36	14.4
91.8	36.4	115.5	120	130	52.0	198	52	20.8
118.5	47.0	82	85	165	66.0	180	70	28.0
147.1	58.4	34	35	215	86.0	173	77	30.8
168.6	66.9	0	0	250	100	165	85	34.0

TABLE 4

Hydrogenation of a Mixture of Mesityl Oxide with Cinnamic Acid in the Presence of Pd
0.74 g of cinnamic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 17°. Pressure 724 mm. Theoretical absorption of hydrogen H_2 249.8 ml $\pi_{1/2} = 1.56$ V

H ₂ absorption		Wave height (mm)	Cinnamic acid			Mesityl oxide		
(ml)	(%)		$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)	$C \cdot 10^{-5}$	$\Delta C \cdot 10^{-5}$	Saturation (%)
0	0	400	250	0	0	250	0	0
21.1	8.5	350	219	31	12.4	239	11	4.4
43.3	17.3	288	180	70	28.0	233	17	6.8
68.8	27.5	216	135	115	46.0	227	23	9.2
91.8	36.7	155	97	153	61.2	219	31	12.4
118.5	47.4	78	49	201	80.4	214	36	14.4
147.1	58.9	0	0	250	100	205	45	18.0

2. Hydrogenation of a mixture of mesityl oxide with maleic acid in the presence of platinum. The polarographic conditions were the same as in the preceding experiment (Table 2, Fig. 2). $S = 0.861$.

3. Hydrogenation of a mixture of mesityl oxide with fumaric acid in the presence of palladium. The polarographic conditions were the same as in the preceding experiments (Table 3, Fig. 3). $S = 0.621$.

4. Hydrogenation of a mixture of mesityl oxide with cinnamic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml 0.1 N NH_4Cl in 96% ethanol for the polarographic analysis. In these conditions cinnamic acid gives a wave but mesityl oxide does not (Table 4, Fig. 4). $S = 0.802$.

TABLE 5

Hydrogenation of a Mixture of Mesityl Oxide with Oleic Acid in the Presence of Pd

1.41 g of oleic acid, 0.49 g of mesityl oxide; 210 mg of Al; 64 mg of Pd, 40 ml of alcohol. Bath temperature 40°, air 22°. Pressure 720 mm. Theoretical absorption of hydrogen H_2 255.5 ml $\pi_{1/2} - 1.23$ V

H ₂ absorption		Wave height (mm)	Mesityl oxide			Oleic acid		
(ml)	(%)		C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)	C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)
0	0	95	250	0	0	250	0	0
21.1	8.2	79	209	41	16.4	250	0	0
43.3	17.0	57	165	85	34.0	250	0	0
66.8	26.1	42	119	131	52.4	250	0	0
91.8	35.9	34	90	160	64.0	230	20	8.0
118.5	46.4	22	58	192	76.8	210	40	16.0
143.1	56.0	10	27	223	89.2	193	57	22.8

TABLE 6

Hydrogenation of a Mixture of Mesityl Oxide with Oleic Acid in the Presence of Pt

1.41 g of oleic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 40°, air 28°. Pressure 715 mm. Theoretical absorption of hydrogen H_2 262.5 ml

H ₂ absorption		Wave height (mm)	Mesityl oxide			Oleic acid		
(ml)	(%)		C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)	C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)
0	0	180	250	0	0	250	0	0
22.7	8.7	150	208	42	16.8	249	1	0.4
46.0	17.5	125	174	76	30.4	238	12	4.8
70.9	27.0	105	146	104	41.6	223	27	10.8
96.4	36.7	90	125	125	50.0	191	59	23.6
123.6	47.1	80	111	139	55.6	154	96	38.4
152.2	58.0	70	97	153	61.2	113	137	54.8
183.0	69.7	59	82	168	67.2	69	181	72.4
216.3	82.4	50	69	181	72.4	19	231	92.4
231.2	88.1	43	60	190	76.0	0	250	100

TABLE 7

Hydrogenation of a Mixture of Mesityl Oxide with Itaconic Acid in the Presence of Pd

0.65 g of itaconic acid, 0.49 g of mesityl oxide; 210 mg of Al, 64 mg of Pd; 40 ml of alcohol. Bath temperature 25°, air 17°. Pressure 722 mm. Theoretical absorption of hydrogen H_2 250.4 ml $\pi_{1/2} - 0.81$ V

H ₂ absorption		Wave height (mm)	Itaconic acid			Mesityl oxide		
(ml)	(%)		C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)	C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)
0	0	175	500	0	0	500	0	0
29.5	11.8	170	486	14	2.8	396	104	20.8
52.6	21.0	165	471	29	5.8	319	181	36.2
79.0	31.6	155	443	57	11.4	241	259	51.8
104.0	41.6	150	429	71	14.2	155	345	69.0
130.7	52.3	145	414	86	17.2	63	437	87.4
159.3	63.7	127	363	137	27.4	0	500	100
171.6	68.6	110	314	186	37.2	0	500	100

5. Hydrogenation of a mixture of mesityl oxide with oleic acid in the presence of palladium. 1 ml of each sample was dissolved in 50 ml of 0.1 N NH_4Cl in 50% ethanol (Table 5, Fig. 5). $S = 0.850$.

6. Hydrogenation of a mixture of mesityl oxide with oleic acid in the presence of platinum. The polarographic conditions were the same as in the preceding experiment (Table 6, Fig. 6). During the first half of the process, mesityl oxide is preferentially saturated, with oleic acid being saturated at the same time but more slowly;

near the end of the relative hydrogenation rate of oleic acid increases so much that its saturation is complete before that of mesityl oxide.

TABLE 8

Hydrogenation of a Mixture of Mesityl Oxide with Itaconic Acid in the Presence of Pt

0.65 g of itaconic acid, 0.49 g of mesityl oxide; 210 mg of Al, 116 mg of Pt; 40 ml of alcohol. Bath temperature 27°, air 30°. Pressure 713 mm. Theoretical absorption of hydrogen H₂ 265 ml

H ₂ absorption		Wave height (mm)	Itaconic acid			Mesityl oxide		
(ml)	(%)		C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)	C · 10 ⁻⁵	ΔC · 10 ⁻⁵	Saturation (%)
0	0	100	250	0	0	250	0	0
21.1	8.0	87.5	219	31	12.4	241	9	3.6
42.3	16.3	75	188	62	24.8	230	20	8.0
66.8	25.2	62.5	156	94	37.6	218	32	12.8
91.8	34.6	50	125	125	50.0	202	48	19.2
118.5	44.7	37.5	94	156	62.4	182	68	27.2

7. Hydrogenation of a mixture of mesityl oxide with itaconic acid in the presence of palladium. 1 ml of each sample was dissolved in 25 ml of 0.1 N HCl in 50 % ethanol. Mesityl oxide does not give a wave in these conditions (Table 7, Fig. 7). The selectivity index in this case had the value S = 0.798.

8. Hydrogenation of a mixture of mesityl oxide with itaconic acid in the presence of platinum. 1 ml of each sample was dissolved in 50 ml of the background solution. Otherwise the polarographic conditions were the same as in the preceding experiment (Table 8, Fig. 8).

Thus, in mixtures of mesityl oxide with maleic, fumaric, and cinnamic acids in the presence of palladium, the first to be hydrogenated, in accordance with Lebedev's rule, are disubstituted ethylene derivatives: maleic acid — almost strictly selectively, and the others not so strictly selectively; in mixtures with oleic and itaconic acids, contrarily to Lebedev's rule, mesityl oxide is hydrogenated first. In presence of platinum hydrogenation is also not strictly selective, the disubstituted derivatives being preferentially hydrogenated in mixtures with maleic and itaconic acids; in the mixture with oleic acid, mesityl oxide is hydrogenated more rapidly at first, but later it is overtaken by oleic acid.

SUMMARY

It was established by polarography that mesityl oxide in mixtures with disubstituted ethylenes is either hydrogenated first, contrarily to Lebedev's rule, or second, in accordance with Lebedev's rule, according to the nature of the other component of the mixture and the nature of the catalyst. The selectivity also varies within fairly wide limits according to these factors, and is selective in only one of a number of mixtures studied.

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* T. p. = C. B. Translation pagination.

POLAROGRAPHIC INVESTIGATION OF PAPAVERINE

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It is known that papaverine is a substituted derivative of benzylisoquinoline which occurs in opium.

The methods for the quantitative determination of this alkaloid are not numerous and not specific; study of the polarographic determination of this alkaloid is therefore of some interest.

Hamamoto [1] first studied this alkaloid with the aid of the dropping mercury electrode in order to determine the so-called electrochemical adsorption coefficient in KCl solution (10^{-3} N). This was taken as the molar dilution of papaverine at which the maximum on the oxygen reduction curve was halved. Kirkpatrick [2] described catalytic waves for papaverine.

No polarographic waves for papaverine obtained as the result of its direct reduction could be found in the literature.

Method and Results

The work was carried out with the aid of the Giredmet (M-8) polarograph with a galvanometer having the following characteristics: $S = 1.6 \cdot 10^{-9}$ A/mm, $t = 6$ sec.

The background for the polarographic studies was provided by aqueous and alcoholic solutions of $N(CH_3)_4OH$ of various concentrations.

In the course of the work various capillaries were used: τ from 3 to 8 seconds and m from 0.655 to 0.574 mg/seconds. The papaverine was recrystallized from alcohol and water. Its original solution contained 0.0063 mole of papaverine in 1 liter of 96% ethyl alcohol.

Fig. 1 shows the curves obtained on the addition of the alcoholic papaverine solution to 0.01 N solution of $N(CH_3)_4OH$. This figure shows that when papaverine is added to the background solution, a wave with a maximum appears ($E_{1/2} = -1.92$ V. relative to the saturated calomel electrode), the height of which at first rises linearly with addition of papaverine (Curves 2 and 3). Upon further addition of papaverine the height of the wave remains practically unchanged, which is apparently due to saturation of the alkaline background solution with papaverine (papaverine is very slightly soluble in alkalis). This is confirmed by the fact that when more alkali is added to the solution the height of the papaverine wave falls sharply (Curve 5) and a white flocculent precipitate of papaverine appears in the solution. In addition, it was noted that increased alkalinity of the background lowers the height of the maximum on the volt-ampere curve for papaverine without altering the value of $E_{1/2}$.

As the applicability of aqueous background solutions of $N(CH_3)_4OH$ is limited because of the poor solubility of papaverine, alcoholic solutions were used, in which papaverine is rather more soluble.

Fig. 2 shows volt-ampere curves given by papaverine in 20% aqueous alcoholic solution of $N(CH_3)_4OH$ (0.02 m); $E_{1/2} = -1.95$. The results obtained were used to plot a calibration graph (Fig. 3).

A characteristic feature of these polarographic curves is the complete absence of the maxima which are so characteristic for the aqueous background solution (Fig. 1) of the same concentration.

Fig. 4 shows polarographic waves for papaverine against a background of 0.02 m. $N(CH_3)_4OH$ in 20, 40, and 90% ethyl alcohol. Distinct waves are obtained for papaverine; they are retained at all the alcohol concentrations studied, and the linear relationship between the wave height and the papaverine concentration is also retained.

The dependence of the wave height on the ethyl alcohol concentration is shown in Fig. 5.

In methyl alcohol the nature of the papaverine waves is changed a little, but the linear relationship between the wave height and the papaverine concentration remains (Fig. 6).

Fig. 7 shows the relationship between E and $\log \frac{I}{I_d - I}$ for the papaverine polarographic wave (based on

Fig. 8); Fig. 7 shows that this relationship is represented as a straight line with a slope of 0.115. Thus, the value of α is close to 0.5, which indicates irreversible reduction of papaverine.

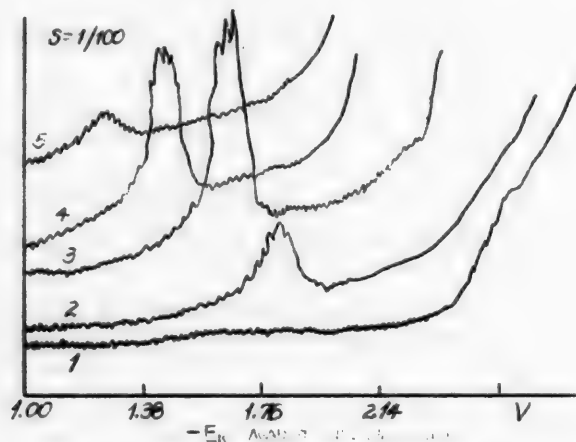


Fig. 1. Polarographic waves for papaverine against a background of $N(CH_3)_4OH$ in water.

1) Background, 10 ml; 2) 0.00022 m; 3) 0.00046 m; 4) 0.00069 m; 5) the last solution with the addition of 0.5 ml of 0.025 N $N(CH_3)_4OH$ solution.

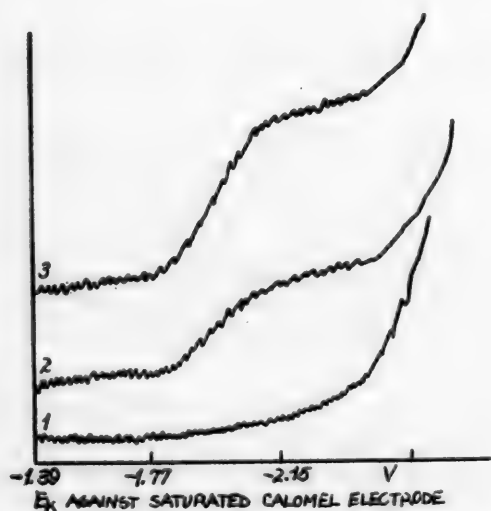


Fig. 2. Polarographic waves for papaverine against background of $N(CH_3)_4OH$ in 20% ethyl alcohol.

1) Background; 2) 0.00023 m; 3) 0.00046 m.

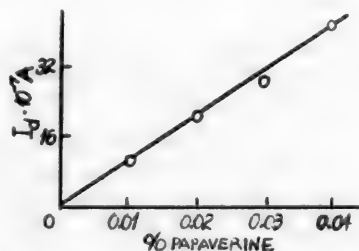
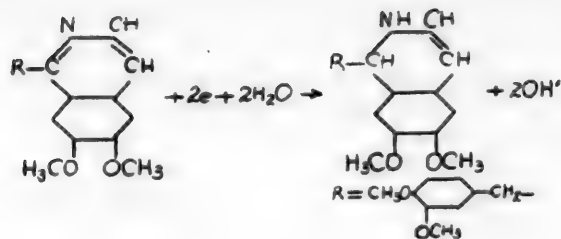


Fig. 3. Calibration graph for papaverine, plotted from the polarographic wave height against background of $N(CH_3)_4OH$ in 20% ethyl alcohol.

Grams taken		Grams found	
Papaverine	Codeine	Papaverine	Codeine
0.0013	0.0018	0.00127	0.00181
0.0011	0.0009	0.00118	0.00094
0.00173	0.0008	0.00163	0.00076
0.0019	—	0.00197	—
0.0004	0.00088	0.00038	0.00087

DISCUSSION

From the structure of the papaverine molecule it may be assumed that its reduction occurs at the double bond between the carbon and nitrogen atoms — the most vulnerable point in the papaverine molecule. As the half-wave potential for papaverine is practically unchanged with change of pH, the reaction of its reduction at the dropping mercury electrode may be represented as follows:



(1)

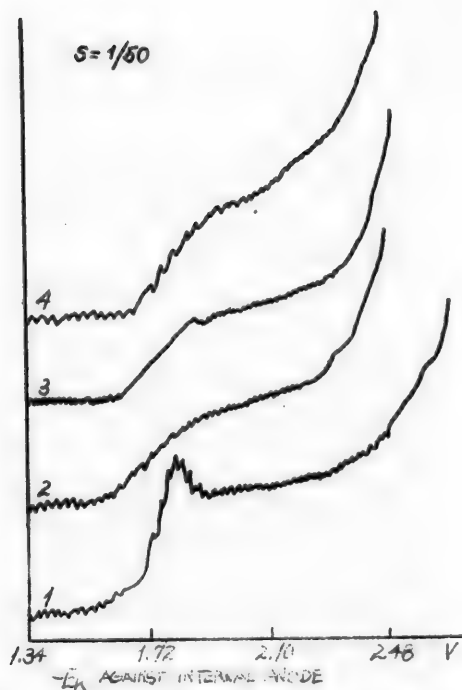


Fig. 4. Polarographic waves for papaverine against a background of 0.02 N $\text{N}(\text{CH}_3)_4\text{OH}$ with various concentrations of ethyl alcohol.

1) In water; 2) in 20% ethyl alcohol; 3) in 40% ethyl alcohol; 4) in 90% ethyl alcohol. Papaverine concentration 0.00096 m.

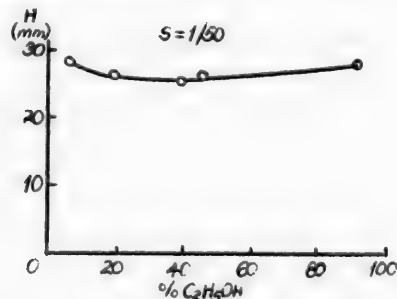


Fig. 5. Variation of the height of the papaverine wave against a background of 0.02 N $\text{N}(\text{CH}_3)_4\text{OH}$ on the concentration of ethyl alcohol.



Fig. 6. Polarographic waves for papaverine against a background of 0.02 N $\text{N}(\text{CH}_3)_4\text{OH}$ in 92% methyl alcohol.

1) Background; 2) 0.0117% papaverine solution; 3) 0.0234% papaverine solution.

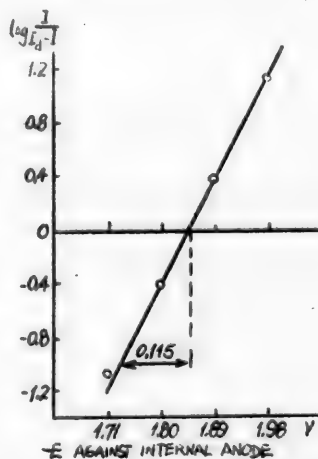
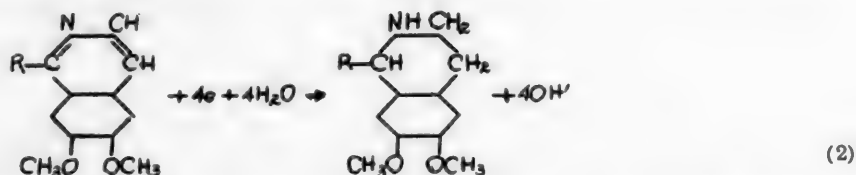


Fig. 7. Relationship between E and $\log \frac{I}{I_d - I}$ for the papaverine wave.

The use of the Ilkovich equation to calculate the diffusion coefficient D for papaverine when $\bar{n} = 2$ gives $D = 0.785 \cdot 10^{-5} \text{ cm}^2/\text{second}$. This value of D is probably much too high, as for caffeine, a substance of much lower molecular weight, $D = 0.62 \cdot 10^{-5} \text{ cm}^2/\text{second}$.

Therefore the reduction reaction probably proceeds not only at the double bond at the nitrogen atom, but also at the second double bond between two carbon atoms. Then not two electrons, as was assumed in the first instance, but four, take part in the reduction reaction:



The value of D obtained with the use of the Ilkovich equation for $\bar{n} = 4$ is $0.20 \cdot 10^{-5} \text{ cm}^2/\text{second}$, which is much closer to reality (by comparison with D for caffeine); therefore the reduction of papaverine at the dropping mercury electrode does apparently require not two but four electrons, and the reaction proceeds according to Equation (2).

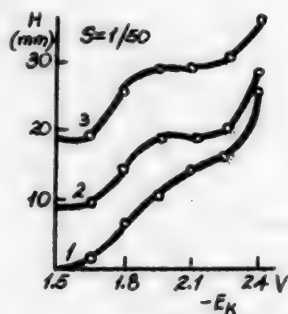


Fig. 8. Results of simultaneous determination of papaverine and codeine.

1) The sum of papaverine (0.0013 g) and codeine (0.0004 g) in 10% ethyl alcohol (volume 15 ml); 2) sum of papaverine (0.0013 g) and codeine (0.0004 g) in 70% ethyl alcohol (codeine wave suppressed); 3) wave for papaverine (0.0013 g) in 70% ethyl alcohol (volume 15 ml).

analyzed polarographically in 70% alcoholic solution, in which the codeine wave (in the concentrations studied, below 0.02 m) does not appear. The results obtained are shown in the table and Fig. 8.

SUMMARY

1. Reduction curves have been obtained for papaverine against a background of 0.02 m solution of $\text{N}(\text{CH}_3)_4\text{OH}$ with a half-wave potential of -1.92 – -1.95 V (against the saturated calomel electrode).

2. It is shown that addition of ethyl alcohol to the background solution improves the form of the polarographic wave for papaverine (the maxima disappear).

3. The mechanism of the reduction of papaverine at the dropping mercury electrode was examined and the values of D and \bar{n} determined.

4. The results obtained are shown to be applicable to the quantitative determination of papaverine in mixtures with codeine.

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This character of the reduction of papaverine is also confirmed by the literature data on the electrochemical reduction of nitrogen-carbon and carbon-carbon (linked to nitrogen) double bonds [3].

The results obtained were used not only for the determination of papaverine in pure solutions, but in mixtures with codeine. This is of definite interest as the half-wave potentials of these two alkaloids are almost the same (for codeine $E_{1/2} = -2.01 \text{ V}$). However, the different polarographic activities of codeine and papaverine in alcohol [4] make it possible to determine each of these alkaloids separately in a mixture by the polarographic method. For this, the total wave height in 10% alcohol is first determined (an alcoholic solution is used in order to increase the solubility of papaverine and at the same time to suppress the maxima on the papaverine wave) and then this mixture is

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FORMATION OF DIPHENYLAMINE CARBOXYLIC ACIDS

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It was previously shown that when N-acylated primary aromatic amines are heated with K_2CO_3 under CO_2 pressure, aminocarboxylic acids and derivatives of 2,4-dioxoquinazoline tetrahydride [1].

Peculiar results were obtained when phenyl isocyanate was used as the N-acylamine. This resulted in the formation, in addition to aminocarboxylic acids and 3-phenyl-2,4-dioxoquinazoline tetrahydride, of diphenylamine and diphenylamine carboxylic acids.

The possibility was not excluded that, in the above process, the formation of diphenylamine carboxylic acids is preceded by the formation of the anilide of a diphenylamine N-carbamic acid (for example, from diphenylamine and phenyl isocyanate) which, analogously to the N-acylated primary aromatic amines, is converted into the corresponding carboxylic acids. In this connection the anilide of diphenylamine-N-carbamic acid was prepared. When this was heated in a stream of CO_2 at 220-240°, diphenylamine-4-carboxylic acid was obtained in approximately 20% yield; when the process was carried out at 180-190°, diphenylamine-N-carbamic acid was formed.

The possibility of preparing the corresponding carboxylic acids from the anilides of diphenylamine 3,3'- and 4,4'-dimethyl-N-carbamic acids was investigated. Only traces of the carboxylic acids were obtained, however. Rather better results were obtained with diphenylamine 2-methyl-N-carbamic acid anilide as the starting material.

When diphenylamine N-carbamic acid anilide was heated with K_2CO_3 under CO_2 pressure, diphenylamine-4,4'-dicarboxylic acid was obtained.

As diphenylamine-4,4'-dicarboxylic acid is not described in the literature, it was of interest to synthesize it by another method. Attempts to prepare this acid by condensation of p-bromobenzoic acid or its esters with the potassium salt or the methyl ester of p-aminobenzoic acid in the presence of copper catalysts were not successful.

Diphenylamine-4,4'-dicarboxylic acid was obtained in quite satisfactory yield by oxidation of 4,4'-dimethyl-N-acetodiphenylamine.

In addition, an interesting method for the synthesis of this acid was found by the action of heat on the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid.

EXPERIMENTAL

Experiments on heating phenyl isocyanate with K_2CO_3

100 g of phenyl isocyanate and 140 g of K_2CO_3 were heated in an autoclave of 400 ml capacity at 200-220° for 8 hours. When the reaction mass reached 150-160°, the pressure rose sharply from 1.5 to 16 atm., and at 200° a pressure of 29-30 atm. was established and maintained till the end. At the end of the experiment the reaction mass was treated with 750 ml of water and filtered. The weight of the precipitate (A) was 10.5-11 g. The filtrate was extracted with benzene and acidified till a mineral acid reaction was obtained, to isolate a mixture of diphenylamine carboxylic acids (B). The filtrate from (B) was neutralized to pH 6.5, extracted with ether, and 1.3-1.4 g of aminobenzoic acid was obtained from the ether extract; after recrystallization from water the acid had m.p. 184-186°, and a sample mixed with p-aminobenzoic acid gave no melting point depression. The precipitate (B) was heated in 220 ml of 70% acetic acid, cooled and filtered (this gave filtrate (C), the treatment of which is described below). The undissolved residue (5.4-5.5 g), m.p. 307-311°, was recrystallized from glacial acetic acid in the form of plates, m.p. 322-324°.

3.630 mg sub.: 8.694 mg CO_2 ; 1.348 mg H_2O . 3.496 mg sub.: 8.389 mg CO_2 ; 1.380 mg H_2O . 4.443 mg sub.: 0.219 ml N_2 (721.2 mm, 21.4°). 4.980 mg sub.: 0.246 ml N_2 (722.0 mm, 21.0°). Found %: C 65.36, 65.48; H 4.16, 4.42; N 5.42, 5.45. $C_{14}H_{11}O_4N$. Calculated %: C 65.4; H 4.28; N 5.44.

When the product was heated in strong sulfuric acid it did not show the fluorescence characteristic for acridone

derivatives, and therefore it did not contain carboxyl groups in the 2 and 2' positions; when heated above its melting point it decomposed with evolution of CO_2 and diphenylamine. A sample mixed with diphenylamine-4,4'-dicarboxylic acid obtained by oxidation of 4,4'-dimethyl-N-acetodiphenylamine melted at 322-324°.

The precipitate (A) was treated with 50 ml of 3% NaOH with warming, cooled, and filtered. The filtrate was acidified till acid to isolate 5.4-5.5 g of a substance which was recrystallized from glacial acetic acid and had m.p. 277-278°. A sample mixed with pure 3-phenyl-2,4-dioxoquinazoline tetrahydride gave no freezing point depression. The substance which did not dissolve in caustic soda (about 4 g) consisted mainly of diphenylamine, which was easily separated by steam distillation (m.p. 53-54°).

The filtrate (C) was diluted with water to give a concentration of 20-25% acetic acid; about 16 g of a resinous substance separated out; when this was washed with water to remove acetic acid, it was converted into a crystalline yellow powder containing diphenylamine p- and o-monocarboxylic acids and certain impurities. To isolate the pure diphenylamine-4-carboxylic acid, the substance was heated to the boil in 80 ml of 25% K_2CO_3 solution, filtered while hot, the precipitate which was deposited from the filtrate was filtered off, washed on the filter with 25% K_2CO_3 solution, treated with dilute hydrochloric acid, filtered again, and washed with water till a neutral reaction was obtained. The result was 5.5-6 g of a substance with m.p. 145-150° which contained diphenylamine-o-carboxylic acid as an impurity, and gave a weak blue fluorescence when heated in concentrated sulfuric acid. To purify the product, it was treated with 40 ml of 14% K_2CO_3 solution and filtered; the filtrate was acidified to isolate 4.5-5 g of a substance which was recrystallized from 50% acetic acid in the form of plates, m.p. 156-157°. The substance gave no fluorescence when heated with concentrated sulfuric acid, and a sample mixed with diphenylamine-4-carboxylic acid (prepared from p-bromobenzoic acid and aniline) of m.p. 157-159°, melted at 157-159°. (The literature gives m.p. 156° for diphenylamine-4-carboxylic acid [2]). The product in sulfuric acid in the presence of nitric acid gave a violet color; when heated above its melting point, it decomposes with evolution of CO_2 and diphenylamine.

Preparation of diphenylamine-4,4'-dicarboxylic acid from 4,4'-dimethyl-N-acetodiphenylamine. 3 g of 4,4'-dimethyl-N-acetodiphenylamine (prepared by heating 4,4'-dimethyldiphenylamine with acetic anhydride, m.p. 84-85°; the literature gives m.p. 85° [3]), 50 ml of water, and 3 g of KMnO_4 were heated together to the boil in a flask fitted with a reflux condenser, with stirring. After half an hour's boiling 4 ml of 15% acetic acid was added (to neutralize the alkali) and 3 g of KMnO_4 , and the mixture was again boiled for 30 minutes, then another 4 ml of 15% acetic acid and another 3 g portion of KMnO_4 were added, the mixture boiled for 30 minutes, another 3 ml of 15% acetic acid added, and the mixture kept at the boil for 30 minutes. The mixture was cooled, made alkaline till a definite reaction to Brilliant Yellow was obtained, and filtered. The filtrate was acidified to isolate a viscous product which was dissolved in 60 ml of 6% KOH and boiled for 3 hours. The liquid was then filtered and the filtrate acidified to isolate about 1.9 g of almost pure diphenylamine-4,4'-dicarboxylic acid; after recrystallization from glacial acetic acid this formed plates, m.p. 322-324°. When heated above the melting point the product decomposed with evolution of CO_2 and diphenylamine. The consumption of alkali corresponds to two carboxyl groups. A sample mixed with the dicarboxylic acid prepared from phenyl isocyanate did not show depression of freezing point.

Preparation of diphenylamine-4,4'-dicarboxylic acid from the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid. 8.5 g of the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid (prepared by exact neutralization of diazoaminobenzene-4,4'-dicarboxylic acid by a solution of caustic potash, followed by evaporation to dryness) was heated to 265-270° and held for several minutes at that temperature. The product, yellow at first, became grey at the end of the reaction; it was treated with 70 ml of water and filtered. The filtrate was acidified to isolate about 4 g of a substance, which was heated to 40-50° with 75 ml of water and 10 g of calcium hydroxide, and then filtered. The filtrate was acidified to isolate the dicarboxylic acid with m.p. 315-317°, which was recrystallized from glacial acetic acid to form plates, m.p. 322-324°. The substance corresponded in all its properties to the dicarboxylic acid prepared from phenyl isocyanate; a mixed sample melted at 322-324°.

Experiments on heating the anilide of diphenylamine-N-carbamic acid with K_2CO_3 in the presence of CO_2 .

Diphenylamine-N-carbamic acid anilide was prepared from diphenylamine and phenyl isocyanate. 127.5 g of diphenylamine was dissolved in 90 g of phenyl isocyanate and left for twenty-four hours; the precipitate was filtered off and washed with alcohol. Crystallization from alcohol gave 113.5 g of a substance with m.p. 136-138°; the mother liquor after recrystallization from toluene gave another 45 g of substance with m.p. 136-138° (136°) [4].

22 g of diphenylamine-N-carbamic acid anilide and 13 g of K_2CO_3 were heated together in a stream of CO_2 in a flask fitted with a stirrer and a reflux condenser (a tube) for 7 hours. In the course of the experiment about 5 g of sublimate collected in the condenser (recrystallization from alcohol gave 4.8 g of diphenylamine with m.p. 54°).

The reaction mass (about 25 g) was treated with 150 ml of water at 40-50°, cooled, filtered, and the filtrate acidified to isolate 2.35 g of diphenylamine carboxylic acid, which was mainly the 4-carboxylic acid with a slight impurity of the 2-carboxylic acid. Crystallization from 20% alcohol gave 2.1 g of diphenylamine-4-carboxylic acid, m.p. 155-157°. A sample mixed with pure diphenylamine-4-carboxylic acid gave no melting point depression.

22 g of diphenylamine-N-carbamic acid anilide and 13 g of K_2CO_3 were heated together in a stream of CO_2 for 2 hours at 190-195°, and then 2.5 hours at 240°. About 3 g of a substance was obtained; after recrystallization from 50% acetic acid this formed plates, m.p. 159-160°, a sample mixed with diphenylamine-4-carboxylic acid (m.p. 157-159°) melted at 159-160°. The substance gave a violet color in sulfuric acid in the presence of nitric acid, and when heated above its melting point decomposed with evolution of CO_2 and diphenylamine.

6.580 mg sub.: 17.684 mg CO_2 ; 2.998 mg H_2O . 6.894 mg sub.: 18.504 mg CO_2 ; 3.174 mg H_2O . 4.480 mg sub.: 0.271 ml N_2 (724.5 mm, 23°). 4.077 mg sub.: 0.254 ml N_2 (723.1 mm, 24°). Found %: C 73.34, 73.24; H 5.10, 5.15; N 6.65, 6.81. $C_{13}H_{11}O_2N$. Calculated %: C 73.24; H 5.16; N 6.57.

1.4 g of diphenylamine-N-carbamic acid anilide and 1.2 g of K_2CO_3 were heated together at 190° for 2 hours. CO_2 was evolved (absorbed by baryta water). The reaction mass was treated with water, when part of the product dissolved. The liquid was filtered and the filtrate was extracted several times with ether. The clear aqueous solution was acidified, and a precipitate of diphenylamine separated out. It is thus clear that the solution contained a salt of diphenylamine-N-carbamic acid, which was decomposed by acid to give diphenylamine.

27 g of diphenylamine-N-carbamic acid anilide and 15 g of K_2CO_3 were heated together under CO_2 pressure (44-46 atm.) at 240-250° for 4 hours. The reaction mass was treated with 200 ml of water, cooled, and filtered. The filtrate was extracted with ether and the aqueous portion was acidified. About 3.7 g of a substance was obtained, which had m.p. 320-322° after double recrystallization from glacial acetic acid. A sample mixed with pure diphenylamine-4,4'-dicarboxylic acid gave no melting point depression.

SUMMARY

1. It is shown that when phenyl isocyanate and K_2CO_3 are heated together under CO_2 pressure, the products are diphenylamine, diphenylamine-4-carboxylic acid, and diphenylamine-4,4'-dicarboxylic acid.
2. It is shown that when diphenylamine-N-carbamic acid anilide is heated with K_2CO_3 in a stream of CO_2 , diphenylamine-4-carboxylic acid is formed, and if the heating takes place under CO_2 pressure, diphenylamine-4,4'-dicarboxylic acid is obtained.
3. It is shown that when the dipotassium salt of diazoaminobenzene-4,4'-dicarboxylic acid is heated, diphenylamine-4,4'-dicarboxylic acid is formed. In view of its simplicity, this method may be of value for preparative purposes.

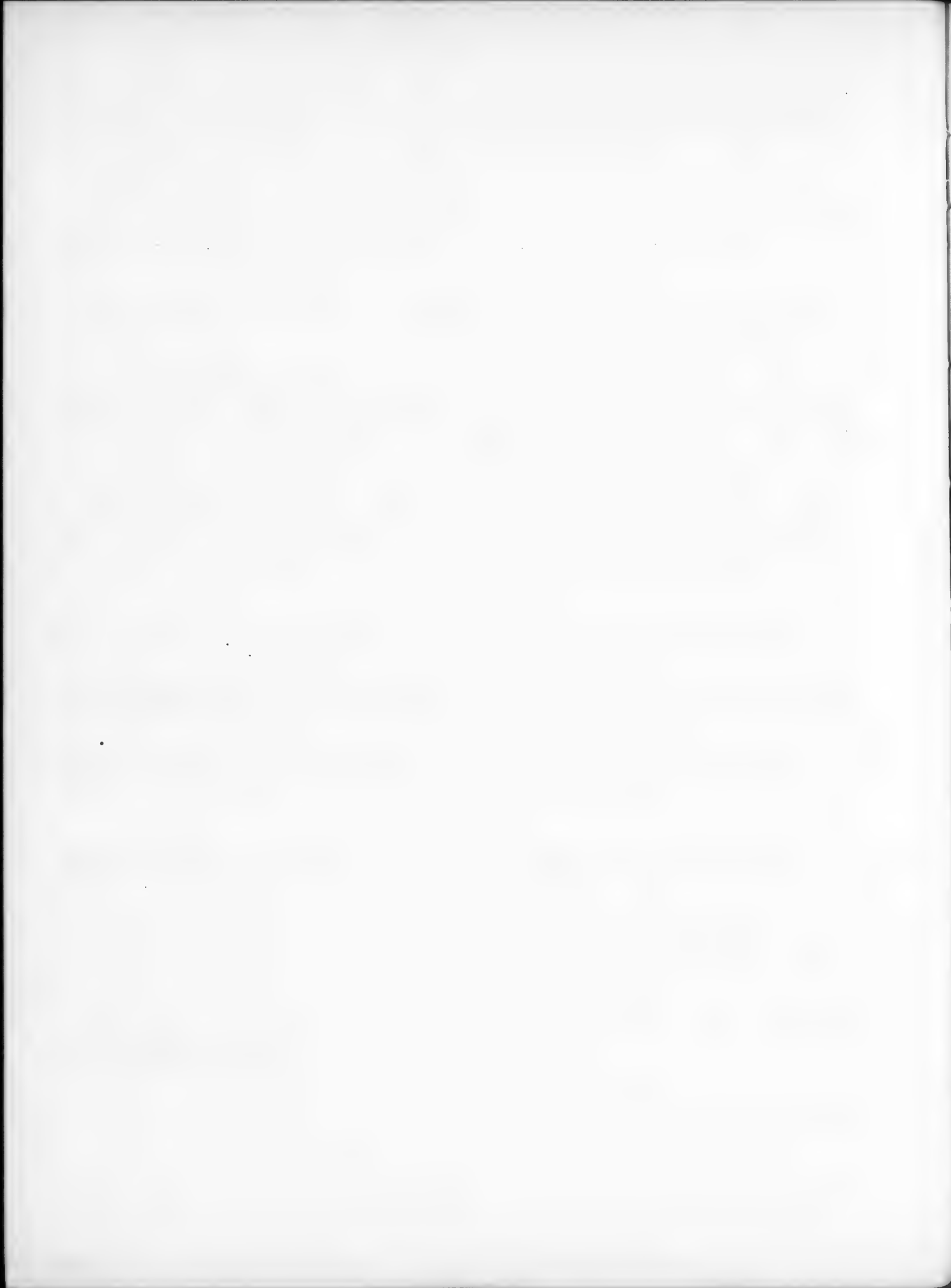
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* T. p. = C. B. Translation pagination.



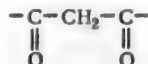
A CHARACTERISTIC REACTION FOR CYCLOPENTADIENE

N. I. Shuikin and V. A. Tulupov

Several qualitative reactions have been proposed for the detection of cyclopentadiene. Vansheidt [1] reported that hydrocarbons containing the $=C-CH_2-C=$ grouping, including cyclopentadiene, when heated in anhydrous acetone or pyridine, give a characteristic color after the addition of one drop of 4 N caustic potash solution in methanol. The color is transient, its shade changes with temperature, and it vanishes when the solution is left to stand in the air.

Terentev and Ivanova [2] proposed two qualitative reactions for the detection of cyclopentadiene in gases. In one of these, cyclopentadiene was evaporated and the vapor was passed in a stream of hydrogen through a solution of mercuric nitrate acidified with nitric acid. It was found that if the gas contained 2% of cyclopentadiene, it was sufficient to pass 2-3 ml of the gas to cause turbidity. However, acetylene gives a similar reaction. Alkenes produce a slight turbidity in the reagent after the gas is passed for 4 minutes, while butadiene has no effect even when passed for 15 minutes through the reagent.

In another reaction, carried out similarly, cyclopentadiene colors a 25% alcoholic solution of benzoquinone intense blue after the addition of several drops of 10% alkali or ammonia solution. However, a similar effect is produced by compounds with labile hydrogen atoms, of the type



An entirely different color is produced by the action of 2-3 drops of concentrated sulfuric acid on a mixture of acetic acid and chloroform containing a small amount of cyclopentadiene [3]. The test is carried out as follows. A drop of cyclopentadiene is dissolved in a mixture of equal volumes (1 ml each) of acetic acid and chloroform. A reddish-violet color is obtained on the addition of 2-3 drops of concentrated sulfuric acid.

Scagliarini and Lucchi [4], who studied the behavior of cyclopentadiene, indene, propylbenzene, naphthalene, retene, and other cyclic hydrocarbons with alkaline methanol solutions of sodium nitroprusside, reported that cyclopentadiene and indene cause reddening of the nitroprusside solution and formation of a red precipitate.

All these reactions were carried out with pure cyclopentadiene, although it is well known that in industry cyclopentadiene is formed as the result of pyrolysis of petroleum products or high temperature coking of coal, and as a result it is always accompanied by alkenes and various dienes.

In the catalytic production of cyclopentadiene from piperylene at 600° and 10-30 mm, its maximum content in the catalyzate does not exceed 9% [5]. Thus, the condensates contain, in addition to cyclopentadiene, the original piperylene and other unsaturated hydrocarbons.

A critical examination of the reactions proposed for the detection of cyclopentadiene shows that they are not specific. The non-specific nature of some of them is pointed out in the literature. For example, Terentev and Ivanova showed, by the use of piperylene as an example, that the reaction with sulfuric acid in a mixture of acetic acid and chloroform is not specific for cyclopentadiene.

The Vansheidt reagent [1] was really proposed not for cyclopentadiene, but for a group of compounds containing labile hydrogen atoms.

In the description of the reaction with sodium nitroprusside [4] it is pointed out that it is not specific, as indene gives a similar color reaction.

We carefully carried out all these reactions with artificial mixtures of cyclopentadiene with piperylene, pentene-1, diisobutenyl, diisocrotyl, and benzene, and we reached the conclusion that with their aid cyclopentadiene can be identified only in the pure state or in mixtures in which its content is not less than 10%. If considerable

amounts of impurities are present (mainly piperylene), none of the proposed reactions reliably detects cyclopentadiene; we therefore attempted to seek a specific reagent by means of which it would be possible to detect cyclopentadiene in mixtures containing not more than 1% of the latter. The following were prepared and tested for their behavior with 90% sulfuric acid containing ferric alum: solutions of 25, 10, and 1% of cyclopentadiene in n-heptane, benzene, piperylene, diisocrotyl, pentene-1, and the pentene mixture obtained by dehydration of isoamyl alcohol.

In addition to the binary mixtures, a ternary mixture was also tested, containing 50% of piperylene, 49% of pentene-1, and 1% of cyclopentadiene.

The tests lead to the conclusion that 90% sulfuric acid containing a small amount of ferric alum is a specific reagent for cyclopentadiene for detecting it in small amounts.

Method of Detection

To prepare the reagent, 100 ml of pure 90% sulfuric acid was saturated with 3 g of finely powdered crystalline ferric alum by periodic shaking for half an hour. After the suspension formed settles, the reagent may be used for the detection of cyclopentadiene. In the solution of ferric alum in sulfuric acid obtained in this way, the iron content is 0.02%.

The qualitative test is carried out by placing 1 ml of the reagent in a test tube, and then adding 1-1.5 ml of the mixture under test down the walls of the tube, so that not less than 0.01 g of cyclopentadiene reacts with the reagent. The test tube is shaken carefully and left to stand about 10 minutes. The reagent becomes almost black with a dark green fluorescent shade by reflected light, and opaque flakes appear on the walls of the tube.

As was to be expected, n-heptane does not react with the reagent, while benzene, pentene-1, and the pentene mixture turn slightly yellow. Piperylene, diisocrotyl, and diisobutenyl give a red color with crimson to cherry-red shades. The results obtained in tests of cyclopentadiene solutions with 25, 10, and 1% contents respectively are shown in the table.

Solvent	Percentage of cyclopentadiene	Color
n-Heptane	25	Black, with dark green fluorescence
	10	
	1	
Benzene	25	Black, with dark green fluorescence
	10	
	1	
Pentene-1	25	As with benzene and n-heptane
	10	
	1	
Mixture of pentenes	25	As with benzene and n-heptane
	10	
	1	
Piperylene	25	As with benzene and n-heptane
	10	
	1	
50% piperylene and 49% pentene-1	1	Dark brown with fluorescence

As the table shows, 1% cyclopentadiene is reliably detected in all mixtures. The other dienes tested (diisocrotyl, diisobutenyl) give the same color as does piperylene.

If the solvent does not react with the reagent, as n-heptane, cyclopentadiene may be detected in amounts down to 0.1 mg in 1 ml of the solution tested.

If the specific black coloration with a fluorescence is not clearly seen, as may happen when the content of cyclopentadiene in piperylene is close to 1%, water should be added and the test tube shaken in order to ascertain definitely whether the mixture contains cyclopentadiene. After the tube has stood for some time, flakes appear in

the aqueous solution, the colors of which depend on the concentration of the cyclopentadiene polymers and their degree of dispersion, while the aqueous layer acquires a pale green color with a violet tinge.

SUMMARY

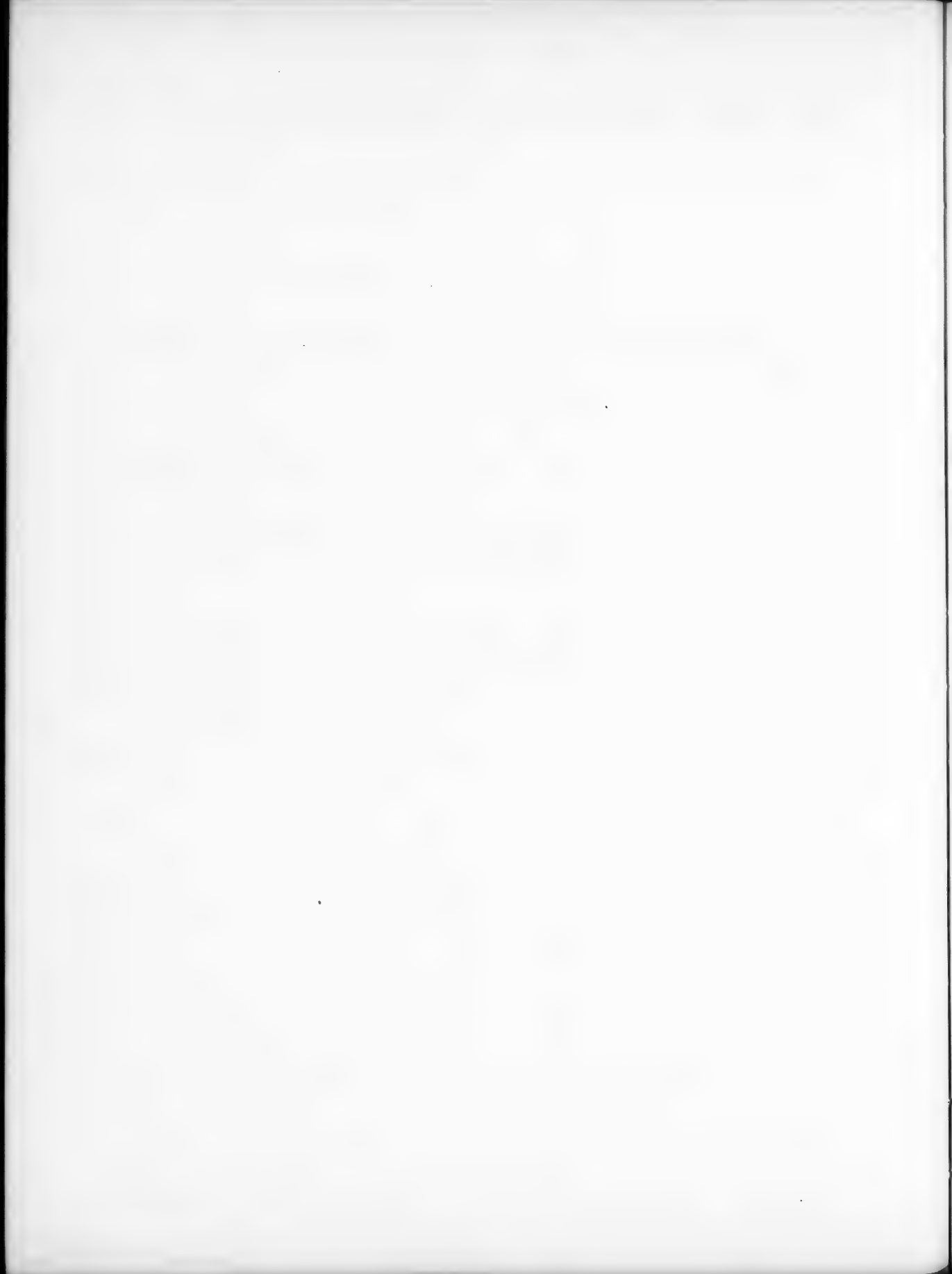
90% sulfuric acid containing a small amount of ferric alum is a specific sensitive reagent for cyclopentadiene.

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INVESTIGATIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

III. THE PREPARATION OF TRIMETHYL- AND TRIETHYL SILANOLS AND THEIR TRANSFORMATIONS

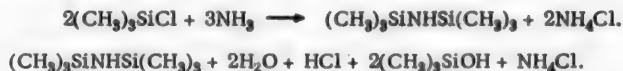
M. F. Shostakovskiy, I. A. Shikhiev, D. A. Kochkin, and V. I. Belyaev

Alkyl or aryl silanols, and in particular trialkyl or triaryl silanols with the general structure $R_3\text{SiOH}$, where R is an alkyl or aryl group, are highly reactive compounds which react with vinyl ethers to give new oxygen-containing organosilicon compounds — organosilicon acetals [1, 2]. The trialkyl or triaryl silanols are intermediates for the preparation of a number of other new compounds. The existing methods for the preparation of the corresponding silanols are still difficult and imperfect, while the properties of these substances are insufficiently well known.

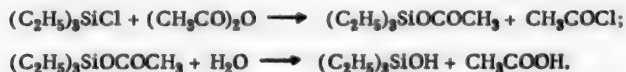
In the present work a study was made of methods for the preparation of trimethyl and triethyl silanols, and also their reactivity with respect to the formation of ethyltrimethyl silane and propyltriethyl silane acetals. This is a continuation of our investigations of oxygen-containing organosilicon compounds [1, 2].

The existence of "silicon hydrates" or silanols was first postulated by D. I. Mendeleev in 1871 in his "Foundations of Chemistry" [3]. Soon after this the first trialkyl silanols were prepared: triethyl silanol [4], tri-n-propyl silanol [5], and triisooamyl silanol [6]. The general method for their preparation was the hydrolysis of the trialkyl halides by caustic soda or ammonia. This method proved unsuitable for the preparation of trimethyl silanol, as it yielded hexamethyl disiloxane instead of the expected trimethyl silanol. The latter was prepared in 1944 from trimethylsilane chloride and gaseous ammonia with the intermediate formation of hexamethyl disilanamine and its subsequent hydrolysis in the presence of mineral acid [7]. In addition, it proved possible to prepare trimethyl silanol by the reaction of methyl polysiloxanes with methylmagnesium bromide or methylmagnesium iodide followed by hydrolysis of the reaction products [7].

It was established as the result of our researches and of a comparative evaluation of the existing methods for the preparation of trialkyl silanols that the most suitable method for the preparation of trimethyl silanol is the ammonolysis of trimethyl silane chloride with the formation of hexamethyl disilanamine followed by its hydrolysis in the presence of mineral acids. The yield of trimethyl silanol was 88.8%.



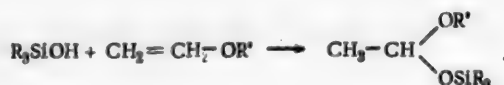
Two methods proved most suitable for the preparation of triethyl silanol: 1) hydrolysis of triethyl silane chloride by caustic soda in ether, and 2) reaction between triethyl silane chloride and acetic anhydride followed by hydrolysis of the acetyl derivative. The hydrolysis takes place in milder conditions and does not result in the formation of hexaethyl disiloxane. The preparation of triethyl silanol by this method may be represented by:



The triethyl silanol yield was 91%.

Trialkyl and triaryl silanols, and also mixed alkyl aryl silanols, may be considered as derivatives of orthosilicic acid, $\text{Si}(\text{OH})_4$, in which three hydroxyl groups are replaced by alkyl or aryl radicals. On the basis of such a structure the properties of the alkyl and aryl silanols would be comparable with those of inorganic acids. However, the replacement of three hydroxyl groups in silicic acid by radicals considerably weakens the properties of the remaining hydroxyl hydrogen, and therefore there is reason to compare the properties of silanols with the properties of the corresponding organic alcohols. The hydroxyl hydrogen of such silanols, as is shown below for a number of reactions, has higher mobility than, for example, in tertiary alcohols.

The reaction between trialkyl silanols, and in particular trimethyl and triethyl silanols, and vinyl ethers is analogous to the corresponding addition reaction of alcohols with formation of mixed acetals of the following structure:



where R and R' are the corresponding alkyl or aryl radicals. The reaction takes place even at room temperature in the presence of traces of mineral acids, and is exothermic.

Investigations of combinational light scattering spectra showed that trimethyl silanol is associated in the liquid phase due to hydrogen bond formation. The presence of hydrogen bonding is confirmed by cryoscopic investigations. Trimethyl silanol also forms associated complexes in benzene solution.

In addition to the high mobility of the hydroxyl hydrogen, trimethyl silanol also has basic properties: it readily splits off water when heated or simply after prolonged standing with formation of hexamethyl disiloxane:



The strong association of trimethyl and triethyl silanols in the liquid phase, for example in cyclohexane solution, is also postulated by other authors on the basis of a comparison of the enthalpies and entropies of evaporation [8]. A comparison of the molecular weights of trimethyl and triethyl silanols with those of the corresponding saturated alcohols — trimethyl and triethyl carbinols — established their resemblance. Thus, the association limit of trimethyl silanol is between three and four. The association number of trimethyl carbinol is four, which indicates a special form of association into a four-membered ring. On the other hand, triethyl silanol is much less associated than trimethyl silanol or trimethyl carbinol. The lower association of the more highly alkylated alkyl silanols is explained by greater steric hindrance.

The reactivity of the hydroxyl hydrogen in trialkyl silanols was also demonstrated in the reaction of trimethyl silanol with alkali and sodium [11]. A trimethyl silanolate was formed. Despite the fact that the increased reactivity of trialkyl silanols toward alkalis is reported in the literature, we must point out that this refers mainly to trimethyl silanol. This reaction practically does not occur with other trialkyl silanols, including triethyl silanol. Triethyl silanolate is formed only in the reaction of triethyl silanol with metallic sodium. However, in this instance also, the formation of the triethyl silanolate indicates the reactive nature of the hydroxyl hydrogen in triethyl silanol.

Trimethyl and triethyl silanols were used for the preparation of ethyltrimethyl silane acetal (I) and n-propyl-triethyl silane acetal (II):



EXPERIMENTAL

1. Preparation of hexamethyldisilamine. 109 g of trimethylchlorosilane (b.p. 56-58°) and 500 ml of dry ether were placed in a two-necked flask of 1 liter capacity, fitted with a gas inlet tube and a reflux condenser the upper end of which was connected to a trap immersed in freezing mixture. The reaction flask was placed on a water bath at a temperature of 0-+7° and a stream of dry ammonia was passed for 9 hours through the solution. The passage of ammonia produced a white precipitate and the mixture became very slightly heated. At the end of the reaction the ether solution was decanted from the ammonium chloride precipitate and filtered. The precipitate was washed several times with dry ether. The ether extracts were combined with the main filtrate and distilled from a Favorsky flask. 52 g of hexamethyldisilamine (64.2%) was collected after removal of the ether.

B.p. 123-125.6° (757 mm), d_4^{20} 0.7764, n_D^{20} 1.4090, MR_D 51.36; calc. 51.23.

Found %: C 44.71, 44.97; H 11.99, 11.73; Si 35.34, 35.30; N 8.68. M 164. $C_6H_{16}NSi$. Calculated %: C 44.67; H 11.87; Si 34.72; N 8.70. M 161.34.

2. Preparation of trimethyl silanol. 70 g of hexamethyldisilanamine, 50 ml of water, 250 ml of ether, and 10 drops of methyl orange were placed in a three-necked flask fitted with a stirrer with a glycerol seal, a reflux condenser, and a dropping funnel. The reaction flask was placed on a water bath at a temperature of 0-+ 7°, and 250 ml of N hydrochloric acid solution was added from the dropping funnel. The reaction was completed in 2.5 hours, as was shown by a change in the color of the methyl orange. The ether layer was separated off in a separating funnel and dried with potash. The product was distilled under normal pressure from a Favorsky flask. 69 g (88.8%) of trimethyl silanol was obtained.

B.p. 98-98.6° (757 mm), n_D^{20} 1.3892, d_4^{20} 0.8139, MR_D 26.22; calc. 26.10.

Found %: C 40.78, 40.75; H 11.19, 11.19; Si 30.85, 30.90. M 92.3. $C_3H_{10}OSi$. Calculated %: C 39.96; H 11.16; Si 31.11. M 90.17.

3. Preparation of triethyl silanol. a) 151.0 g of triethylchlorosilane (b.p. 143.0-144.0° at 753 mm, n_D^{20} 1.4310, d_4^{20} 0.8970) and 102.1 g of anhydrous acetic anhydride (b.p. 140°, n_D^{20} 1.3900, d_4^{20} 1.0800) were placed in a two-necked flask 0.5 liter in capacity, fitted with a thermometer and a reflux condenser with an outlet tube and a thermometer in its upper part. The reaction mixture was heated on an oil bath at the boiling point for 5-6 hours. The acetyl chloride formed in the reaction was driven off through the outlet tube of the condenser. The boiling under reflux was stopped after all the acetyl chloride was driven off, which was determined from the amount of it in a graduated receiver and the increase in the vapor temperature of the reaction mixture. The residue in the flask after removal of the acetyl chloride was introduced dropwise from a dropping funnel under a layer of aqueous ammonia with constant stirring (500 ml of water and 20 ml of 18% ammonia). The temperature of the reaction mixture did not exceed + 6°. The triethyl silanol formed floated as an oily layer. This was separated from the aqueous layer, washed with two portions of water, dried over potash, and fractionated from a Favorsky flask. This gave 99.2 g (75%) of triethyl silanol.

B.p. 80° (30 mm), 153.5-154.5° (753 mm), n_D^{20} 1.4341, d_4^{20} 0.8646.

Found %: C 54.32, 54.45; H 12.13, 12.17; Si 21.20, 21.25. C_3H_8OSi . Calculated %: C 54.50; H 12.19; Si 21.22.

b) 100.0 g of triethylchlorosilane (b.p. 143.0-144.0° at 753 mm, d_4^{20} 0.9220), 500 ml of anhydrous ether, and several drops of phenolphthalein were placed in a three-necked flask 1.0 liter capacity, fitted with a mechanical stirrer and a dropping funnel. The reaction mixture was cooled to -5° and N NaOH solution was added with vigorous stirring until a permanent pale pink color was produced. The temperature of the reaction mixture did not exceed + 2°. The ether layer was then separated from the aqueous layer and dried with potash. After removal of the ether the reaction mixture was fractionated under vacuum and the fraction with b.p. 76-80° (30 mm) was isolated. A second fractionation yielded 68.8 g (91%) of a substance with the following constants:

B.p. 80° (30 mm), n_D^{20} 1.4340, d_4^{20} 0.8645, MR_D 39.85; calc. 40.08.

Triethyl silanol is a mobile colorless liquid with a camphor-like smell, partially soluble in water, easily soluble in organic solvents. It can be kept for a long time in a glass flask with a ground glass stopper. Strong heating in the presence of mineral acids converts it into hexaethyl disiloxane. It does not react with solutions of alkalis. It reacts vigorously with metallic sodium or potassium on heating.

4. Synthesis of ethyltrimethylsilane acetal. (Jointly with V. M. Vlasov). An ampoule cooled to -8° was filled with 22.5 g of trimethyl silanol (b.p. 98.0-99.0°, n_D^{20} 1.3892, d_4^{20} 0.8139), 21 g of vinyl ethyl ether (b.p. 36.0-37.0°, n_D^{20} 1.3776, d_4^{20} 0.7730) and 0.004 g of concentrated hydrochloric acid. The sealed ampoule was heated in a thermostat at 65° for 8 hours. After treatment of the reaction product with calcined potash and distillation from a Favorsky flask fitted with a trap cooled by ice and salt, the following fractions were isolated: 1st to 21° (17 mm), 23.4 g, n_D^{20} 1.3825; 2nd 37-38° (17 mm), 6.8 g, n_D^{20} 1.3937; residue 2.3 g. The 8.3 g of the product collected in the trap was added to the 1st fraction and treated with metallic sodium. Distillation of the 1st fraction under atmospheric pressure gave 18.4 g of a product with b.p. 99-100°, n_D^{20} 1.3784, d_4^{20} 0.7632, and 5.4 g of a product with b.p. 102-104°, n_D^{20} 1.3806, d_4^{20} 0.8236. These data indicate that the product with b.p. 99-100° is hexamethyl disiloxane, and the product with b.p. 102-104° is the symmetrical diethyl acetal •.

* Literature data for hexamethyl disiloxane: b.p. 98.5° (740-760 mm), n_D^{25} 1.3730, d_4^{25} 0.756 [9]; for the symmetrical diethyl acetal: b.p. 103-104°, n_D^{20} 1.3820, d_4^{20} 0.8254 [10].

A second fractionation of the 2nd fraction with b.p. 37-38° (17 mm) yielded 6.2 g of a product with the following constants:

B.p. 38-39° (16-17 mm), n_D^{20} 1.3940, d_4^{20} 0.8346, MR_D 46.43; calc. 46.70.

Found %: C 51.90, 52.01; H 11.37, 11.47; Si 16.80, 17.80. M 154.5, 158.2. $C_7H_{18}O_2Si$. Calculated %: C 51.79; H 11.18; Si 17.29. M 162.2.

These results correspond to ethyltrimethylsilane acetal; the yield was 15.3% on the original trimethyl silanol. The product is a transparent liquid with a faint ethereal smell; it is insoluble in water, and readily soluble in alcohol, acetone, ether, and chlorinated hydrocarbons.

5. Synthesis of n-propyltriethylsilane acetal. A wide necked ampoule was filled with 33 ml of triethyl dilanol (b.p. 80° at 30 mm, n_D^{20} 1.4332, d_4^{20} 0.8645) and 21.5 g of vinyl n-propyl ether (b.p. 65.0-65.3°, n_D^{20} 1.3920, d_4^{20} 0.7678). 0.02 ml of 30% hydrochloric acid was added to the mixture. The temperature of the contents of the ampoule gradually rose to 40° on shaking. The ampoule was then sealed and heated in a thermostat at 65° for 10 hours. On the following day the ampoule was opened, the contents dried over potash, and distilled under vacuum; this yielded 46 g of a fraction with b.p. 91-92° (14 mm), n_D^{20} 1.4254. A second distillation gave 35 g of a product with the following constants:

B. p. 89-90° (13-14 mm), 204-205° (760 mm), n_D^{20} 1.4250, d_4^{20} 0.8572, MR_D 65.03; calc. 65.22.

Found %: C 60.21, 60.10; H 12.13, 11.95; Si 13.50, 13.88. $C_{11}H_{26}O_2Si$. Calculated %: C 60.49; H 12.00; Si 12.84.

This substance was n-propyltriethylsilane acetal, the yield being 67.45% calculated on the triethyl silanol taken. It is a colorless liquid with an ethereal odor, soluble in alcohol, ether, acetone, chlorinated and aromatic hydrocarbons, insoluble in water.

SUMMARY

1. Methods for the preparation of trimethyl and triethyl silanols in good yields have been modified and improved.
2. The following organosilicon acetals have been obtained for the first time: ethyltrimethylsilane acetal, by the reaction of vinyl ethyl ether with trimethyl silanol, and n-propyltriethylsilane acetal, by the reaction of vinyl propyl ether with triethyl silanol.

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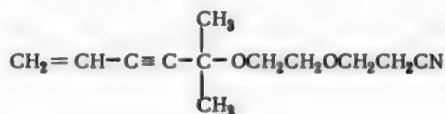
CONDENSATION OF DIMETHYLVINYLETHYNYL CARBINOL WITH ETHYLENE OXIDE

E. S. Lagucheva

As was reported previously [1, 2], when dimethylethynyl carbinol is heated in an autoclave with alkylene oxides in the presence of tertiary organic compounds, the corresponding β -hydroxyalkyl ethers are formed in good yields. It was desired to verify the applicability of this method to the preparation of the β -hydroxyethyl ether of dimethylvinylethynyl carbinol, especially because this compound is obtained in low yields by the previously described methods [3, 4] for its synthesis.

When the condensation of dimethylvinylethynyl carbinol with ethylene oxide was carried out in the presence of dimethylaniline, the β -hydroxyethyl ether of dimethylvinylethynyl carbinol was obtained. The use of dimethylaniline as a catalyst, which also acted as a polymerization stabilizer, proved very successful in completely preventing resin formation.

The β -hydroxyethyl ether of dimethylvinylethynyl carbinol was identified by conversion into the β -cyanoethoxyethyl ether of dimethylvinylethynyl carbinol *.



EXPERIMENTAL

β -Hydroxyethyl ether of dimethylvinylethynyl carbinol. 330 g (3 moles) of the freshly distilled carbinol, 44 g (1 mole) of ethylene oxide, and 11.6 g (3.5% on the carbinol) of dimethylaniline were placed in an autoclave fitted with a manometer. The autoclave was placed in an oil bath, and the reaction was continued for 7 hours at a bath temperature of 60-85°; no increase of pressure was observed. At the end of the process the excess carbinol (252 g) was removed from the reaction mixture under vacuum with the aid of a fractionating column. The residue was fractionated under vacuum from a Claisen flask; the following main fractions were obtained: 1st, b.p. 80-82° (4 mm), 75.5 g; 2nd, b.p. 114-116° (4 mm), 7 g.

The first fraction, obtained in 69.2% yield, had the following data:

d_{20}^{20} 0.9515, n_D^{20} 1.4797 (n_D^{15} 1.4819), M_{rD} 45.9; calc. 44.46.

Found %: OH 10.46, 10.67 (phthalation). $C_9H_{14}O_2$. Calculated %: OH 11.03.

By its boiling range and refractive index this fraction corresponded to the β -hydroxyethyl ether of dimethylvinylethynyl carbinol, for which the literature gives: b.p. 80-81° at 4 mm, n_D^{15} 1.4811 [4], n_D^{17} 1.4820 [3].

The 2nd fraction, b.p. 114-116° at 4 mm, corresponded to the glycol ether of dimethylvinylethynyl carbinol (yield 6.4%), for which the literature gives: b.p. 103-104° at 2 mm, n_D^{15} 1.4811.

β -Cyanoethoxyethyl ether of dimethylvinylethynyl carbinol. 31 g (0.2 mole) of the β -hydroxyethyl ether of dimethylvinylethynyl carbinol was mixed with 1.86 g of 40% aqueous caustic soda solution, and 12 g (0.22 mole) of acrylonitrile was then added to the solution heated to 30°. The process was continued 4 hours at 30-35°. At the end of the reaction the product was separated from the aqueous layer, neutralized with dilute hydrochloric acid, and fractionated under vacuum. 4 g of the original β -hydroxyethyl ether of dimethylvinylethynyl carbinol was driven off. The β -cyanoethoxyethyl ether of dimethylvinylethynyl carbinol was collected in the range 129-131° at 3 mm. It was a pale, mobile, easily polymerized liquid. The yield was 21 g of the β -cyanoethoxyethyl ether of

* In our paper on the cyanoethylation of acetylenic alcohols [5], the source [6] in which the cyanoethylation of dimethylethynyl carbinol was described, was omitted.

dimethylvinylethynyl carbinol, which was 60% calculated on the β -hydroxyethyl ether of dimethylvinylethynyl carbinol which entered the reaction.

d_{20}^{20} 0.9709, n_D^{20} 1.4636, MR_D 58.80; calc. 57.97.

0.2672 g sub.: 13.68 ml 0.1 N H_2SO_4 . 0.3297 g sub.: 16.46 ml 0.1 N H_2SO_4 . Found %: N 7.17, 6.99. $C_{12}H_{17}O_2N$. Calculated %: N 6.76.

SUMMARY

1. It is shown that when dimethylvinylethynyl carbinol is heated with ethylene oxide in an autoclave in the presence of dimethylaniline, the β -hydroxyethyl ether of dimethylvinylethynyl carbinol is formed in good yield.
2. The synthesis of the β -cyanoethoxyethyl ether of dimethylvinylethynyl carbinol is described.

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STUDY OF TAUTOMERIC COMPOUNDS

XVII. THE REACTION OF DIAZO COMPOUNDS WITH CONDENSATION PRODUCTS OF PHENYLMETHYLPYRAZOLONE AND KETONES

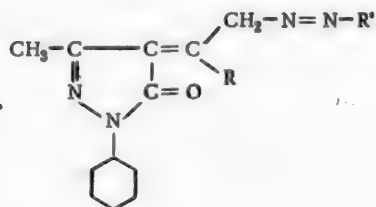
A. E. Poraj-Koshits* and M. S. Dinaburg

As was already reported, the condensation products of phenylmethylpyrazolone and methyl ketones are distinguished by the high mobility of the hydrogen atoms in the methyl groups [1]. Somewhat earlier one of the present authors [2] showed by a number of examples that in the presence of higher hydrogen atom activity in the methyl groups the compounds are capable of entering coupling reactions with diazo compounds.

Such compounds include mesomethylacridine [3], isopropylidene and phenylethylidene derivatives of iso-oxazolones [4], trinitrotoluene [5] and some others [6]. Instances are known when the power to enter this reaction appears only after additional activation of the hydrogen atoms. König [7] was the first to point out that lepidine and quinaldine derivatives are capable of reacting with diazo compounds only in the form of anhydro-bases of the halo-alkyl derivatives. Simple salt formation is sometimes sufficient for this. Indeed, the coupling reaction of mesomethylacridine takes place successfully only in an acetic acid medium, when the mesomethylacridine is present in the form of an oxonium salt [8].

Our investigations showed that phenylmethylpyrazolone derivatives, containing a methyl ketone residue, are also capable of coupling with diazo compounds. The reaction may only be brought about in a mineral acid medium, and apparently the previous formation of an onium salt (through the imino nitrogen of the pyrazolone ring) is just as essential as in the coupling of mesomethylacridine. However, because of the very low basicity of these derivatives they can only form salts with strong mineral acids [9].

In such conditions the reaction with diazo compounds occurs with practically all available diazo compounds and results in the formation of deeply colored compounds, to which we assign the following structure on the basis of their properties and analytical data:



where $R' = \text{aryl}$, and $R = \text{CH}_3, \text{C}_6\text{H}_5$
or $m\text{-NO}_2\text{C}_6\text{H}_4$

The absorption spectra of the compounds formed show considerable intensification of color in comparison with phenylmethylpyrazolone derivatives which do not contain intermediate ketone residues, and, as in the case of condensation products with aldehydes, the presence of two maxima. The position of one of these, in the visible part of the spectrum, is determined by the nature of the side chain; the second maximum, in the ultraviolet region of the spectrum at $\lambda = 250 \text{ m}\mu$ is constant for all the phenylmethylpyrazolone derivatives, and its formation is evidently due to the action of the pyrazolone ring.

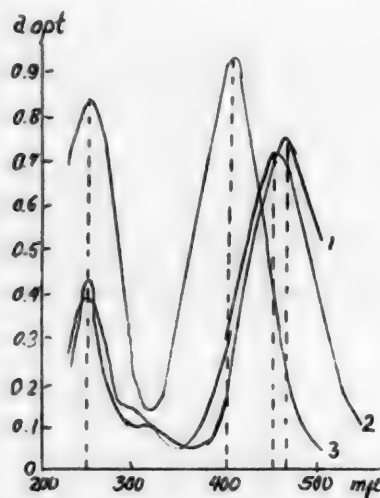
* Deceased.

EXPERIMENTAL

Coupling of 4-isopropylidenephénylmethylpyrazolone with diazo compounds

4-[α -Methyl- β -(phenylazo)]-ethylidenephénylmethylpyrazolone. 0.93 g of aniline in 2 ml of concentrated hydrochloric acid and 1-2 ml of water was diazotized at 0° with 0.7 g of nitrite in 2 ml of water. Urea was added to the diazonium salt solution to remove excess nitrous acid. The diazonium solution was added dropwise at 0° to 2.14 g of isopropylidenephénylmethylpyrazolone in 25 ml of glacial acetic acid and 0.7 ml of concentrated hydrochloric acid. A crystalline precipitate was formed immediately; this was filtered off after 1-1.5 hours, washed with alcohol and dried. Yield 1.8 g (56.6%). The substance formed bright red scales from glacial acetic acid. M.p. 173-174°.

0.1476 g sub.: 22.5 ml N₂ (17°, 755 mm). 0.1077 g sub.: 16.4 ml N₂ (17°, 756 mm). 0.1067 g sub.: 0.2794 g CO₂; 0.0526 g H₂O. Found %: C 71.40; H 5.46; N 17.85, 17.76. C₁₉H₁₈ON₄. Calculated %: C 71.69; H 5.66; N 17.61.



1) 4-[α -phenyl- β -(phenylazo)ethylidene]-1-phenyl-3-methylpyrazolone-5; 2) 4-[α -methyl- β -(phenylazo)ethylidene]-1-phenyl-3-methylpyrazolone-5; 3) 4-phenyl-azo-1-phenyl-3-methylpyrazolone-5.

4-[α -Methyl- β -(4'-nitrophenyl)-azo]-ethylidenephénylmethylpyrazolone. This was obtained in a manner analogous to the above from 2.14 g of isopropylidenephénylmethylpyrazolone in 50 ml of glacial acetic acid and diazotized p-nitroaniline. Yield 2.76 g (76%). Crystallization from a large amount of glacial acetic acid gave fine reddish-violet needles, m.p. 234-236°.

0.1437 g sub.: 0.3296 g CO₂; 0.0657 g H₂O. Found %: C 62.57; H 4.50. C₁₉H₁₇O₃N₅. Calculated %: C 62.80; H 4.68.

4-[α -Methyl- β -(2',5'-dichlorophenyl)-azo]-ethylidenephénylmethylpyrazolone. 2.14 g of isopropylidenephénylmethylpyrazolone was dissolved in 50 ml of glacial acetic acid and 1.0 ml of hydrochloric acid ($d = 1.19$). A solution of freshly prepared zinc chloride diazonium double salt, obtained from 1.62 g of dichloroaniline, in 15 ml of water, was added to the thoroughly cooled solution with stirring. Separation of a crystalline precipitate commenced immediately. The precipitate was filtered off after 2.5 hours. Yield 2.0 g (51.4%). The substance crystallized as bright red shiny needles from acetic acid, m.p. 194°.

0.1133 g sub.: 14.2 ml N₂ (18°, 767 mm). Found %: N 14.80. C₁₉H₁₆ON₄Cl₂. Calculated %: N 14.47.

4-[α -Methyl- β -(3'-carboxyphenyl)-azo]-ethylidenephénylmethylpyrazolone. To a solution of 2.14 g of isopropylidenephénylmethylpyrazolone in 25 ml of glacial acetic acid and 1.0 ml of concentrated hydrochloric acid a solution of the diazo compound obtained from 1.37 g of m-aminobenzoic acid was added with cooling and stirring. The reaction is rather slow, and the addition was regulated so as to avoid accumulation of the diazo compound in the solution. A copious crystalline precipitate began to form 30 minutes after all the diazo solution had been added. Yield 1.74 g (49.1%). Crystallization from a large amount of acetic acid gave violet-red crystals, m.p. 235-236°. Careful dilution of the mother liquor with 30 ml of water yielded a further 0.5-0.6 g of the substance. The total yield was 2.27 g (62%).

0.1734 g sub.: 0.4209 g CO₂; 0.0804 g H₂O. Found %: C 66.21; H 5.14. C₂₀H₁₈O₃N₄. Calculated %: C 66.29; H 4.97.

4-[α -Phenyl- β -(2',5'-dichlorophenyl)-azo]-ethylidenephénylmethylpyrazolone. 2.76 g of 4- α -phenylethylidenephénylmethylpyrazolone in 25 ml of glacial acetic acid was mixed with a solution of the zinc chloride double salt of the diazonium compound prepared from 1.6 g of 2,5-dichloroaniline, in 10 ml of water. 0.5 ml of hydrochloric acid ($d = 1.19$) was added dropwise to the pale yellow solution of the two components. Each drop of acid left a brightly colored trace in the solution, and crystallization commenced at once. After a few minutes the

precipitate was filtered off, washed with alcohol, and dried. Yield 4.0 g (87%). Crystallization from a large amount of alcohol gave violet-red leaflets or violet-brown needles, m.p. 185-186°.

0.1279 g sub.: 13.5 ml N₂ (18°, 764 mm). 0.1359 g sub.: 14.3 ml N₂ (18°, 768 mm). 0.1779 g sub.: 0.1080 g AgCl. Found %: N 12.42, 12.50; Cl 15.46. C₂₄H₁₈ON₄Cl₂. Calculated %: N 12.47; Cl 15.80.

4-[α -Phenyl- β -(4'-nitrophenyl)-azo]-ethylidenephénylmethylpyrazolone. 2.76 g of 4-phenylethylidenephénylmethylpyrazolone in 50 ml of glacial acetic acid was coupled with diazotized p-nitroaniline (1.45 g). At the end of the addition of the diazo solution the whole mass congealed into a crystalline slurry. Yield 3.1 g (73.0%). Crystallization from glacial acetic acid gave long green needles or prisms, m.p. 235-236°.

0.1005 g sub.: 0.2509 g CO₂; 0.0462 g H₂O. 0.1082 g sub.: 0.2697 g CO₂; 0.0475 g H₂O. 0.1073 g sub.: 15.2 ml N₂ (20°, 764 mm). Found %: C 68.07, 67.97; H 5.10, 4.47; N 16.65. C₂₄H₁₉O₃N₅. Calculated %: C 67.76; H 4.47; N 16.47.

4-[α -Phenyl- β -(2'-nitro-4'-chlorophenyl)-azo]-ethylidenephénylmethylpyrazolone. 1.73 g of 1-amino-2-nitro-4-chlorobenzene was dissolved in 15 ml of concentrated hydrochloric acid, and the hot solution was poured into ice. 0.69 g of sodium nitrite in 3 ml of water was at once added to the mixture. Urea was added to the solution of the diazo compound formed till a reaction for free nitrous acid was no longer obtained, and the solution was then added dropwise to a solution of 2.76 g of 4- α -phenylethylidenephénylmethylpyrazolone in 50 ml of glacial acetic acid. Almost immediately a precipitate in the form of shining chocolate-colored needles was formed. Yield 2.15 g (47%).

Crystallization from glacial acetic acid gave needles, m.p. 226-227°.

0.1376 g sub.: 0.3130 g CO₂; 0.0505 g H₂O. 0.1553 g sub.: 20.9 ml N₂ (22°, 759 mm). Found %: C 62.03; H 4.07; N 15.52. C₂₄H₁₅O₃N₅Cl. Calculated %: C 62.21; H 3.91; N 15.21.

4-[α -Phenyl- β -phenylazo]-ethylidenephénylmethylpyrazolone. A solution of the diazonium salt from 0.93 g of aniline was added to a solution of 2.76 g of phenylethylidenephénylmethylpyrazolone in 30 ml of glacial acetic acid and 0.5 ml of concentrated hydrochloric acid. The reaction mass turned a ruby-red color. 30 ml of water was added to the mass with thorough stirring. The precipitate formed was separated off after 12 hours. Yield 2.64 g (69.8%). Crystallization from alcohol gave reddish-brown leaflets, m.p. 118-120° (decomp.). When heated for a short time to 100° the color of the crystals changed to blue-black, m.p. 118-120°. The substance decomposed when heated for a long time at 100°.

0.1361 g sub.: 0.3621 g CO₂; 0.0743 g H₂O. 0.1436 g sub.: 0.3825 g CO₂; 0.0773 g H₂O. 0.1088 g sub.: 14.0 ml N₂ (21°, 744 mm). Found %: C 72.54, 72.42; H 6.04, 6.04; N 14.63. C₂₄H₂₀ON₄·H₂O. Calculated %: C 72.36; H 5.87; N 14.05.

4-[α -Phenyl- β -(2'-carboxyphenyl)-azo]-ethylidenephénylmethylpyrazolone. 2.76 g of 4- α -phenylethylidenephénylmethylpyrazolone was dissolved in 50 ml of glacial acetic acid and 1.0 ml of concentrated hydrochloric acid. A solution of the diazo compound from 1.37 g of anthranilic acid was added to the solution with cooling and stirring. After 3 hours the precipitate formed was filtered off, washed with alcohol, and dried. Yield 3.47 g (81.8%). Crystallization from glacial acetic acid gave blue-black needles, m.p. 214-215°.

0.1017 g sub.: 0.2821 g C₂O; 0.0439 g H₂O. Found %: C 75.60; H 4.80. C₂₅H₂₀O₃N₄. Calculated %: C 75.47; H 4.71.

4-[α -(m-Nitrophenyl)- β -(p-nitrophenyl)-azo]-ethylidenephénylmethylpyrazolone. 1.62 g of m-nitrophenylethylidenephénylmethylpyrazolone was mixed with 30 ml of acetone, and 1.5 ml of concentrated hydrochloric acid was added to the suspension. The yellow precipitate dissolved instantly. The diazo solution prepared from 0.69 g of p-nitroaniline containing 0.5 g of urea was added to the faintly yellow solution. The crystals formed were separated off after 1.5 hours and washed with ether. Yield 1.2 g (51.5%). For purification the substance was dissolved in hot pyridine. The ruby-red solution was filtered and diluted with an equal volume of hot water. On cooling, green needles with a bronze tinge separated out, m.p. 231-232°.

0.1161 g sub.: 18.2 ml N₂ (20°, 762 mm). 0.1245 g sub.: 0.2803 g CO₂; 0.0418 g H₂O. Found %: C 61.43; H 3.84; N 18.10. C₂₄H₁₃O₅N₆. Calculated %: C 61.28; H 3.95; N 17.87.

SUMMARY

1. The condensation products of phenylmethylpyrazolone with methyl ketones are capable of reacting with

diazo compounds with the participation of the hydrogen atoms of the methyl groups. This power is displayed only in a mineral acid medium.

2. The increased mobility of the methyl group hydrogens in an acid medium is due to loss of an unshared electron pair by the hetero-nitrogen atom in the ring, and conversion of the substance into an onium salt.

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SYNTHESES AND TRANSFORMATIONS OF PYRIMIDINE DERIVATIVES

V. SULFONATION OF PYRIMIDINE DERIVATIVES

N. V. Khromov-Borisov and R. S. Karlinskaya

By comparison with benzene, pyridine is much less reactive to electrophilic reagents; nitration and sulfonation of pyridine take place with much greater difficulty than in the case of benzene [1]. Because of displacement of the electron cloud to the N hetero-atom, the electron density of all the carbon atoms in the pyridine molecule is decreased. The greatest decrease of electron density is at the α and γ carbon atoms, and therefore the action of electrophilic reagents is directed to the beta-position.

By an extension of this reasoning to the pyrimidine ring it is to be expected that this should be even more inert toward such reagents and that the action of these reagents would be directed to the 5-position.

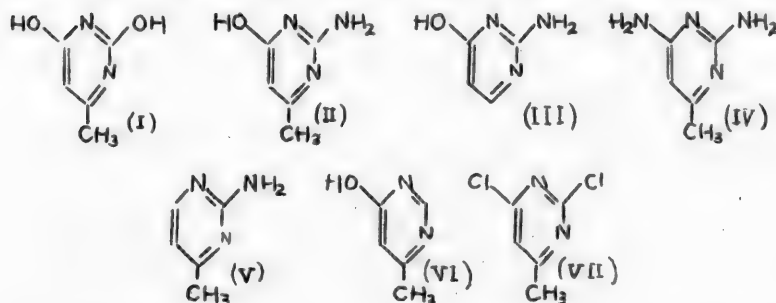
It is not possible either to nitrate or to sulfonate unsubstituted pyrimidine.

Pyrimidine derivatives with 1st type substituents in the 2,4, or 6 positions should, like the corresponding pyridine derivatives, be nitrated and sulfonated more easily. However, while monohydroxy and monoamino derivatives of pyridine are nitrated in definite conditions [2], it is not possible to nitrate pyrimidine derivatives containing a single hydroxyl group or a single amino group in the even-numbered positions in the ring [3]. A nitro group can be introduced into the 5-position by the action of strong nitrating agents only in the presence of two substituents (OH, NH₂) in the even-numbered positions in the pyrimidine ring. This reaction has great practical importance and is widely used for the synthesis of various pyrimidine derivatives.

The literature contains no information on the sulfonation of pyrimidine derivatives. Only one of our earlier papers [4] includes data on sulfonation of 2,6-dihydroxy-4-methylpyrimidine.

In the present investigation a special study was made of the sulfonation of pyrimidine derivatives containing the following substituents in the molecule: OH, NH₂, CH₃, Cl. These substituents were in the 2,4, and 6 positions of the pyrimidine ring and therefore affected mainly the 5 position, to which, as was already stated, the action of electrophilic reagents is directed.

The following pyrimidine derivatives were sulfonated by the action of chlorosulfonic acid on heating:



The compounds (I) [4], (II), (III), and (IV) react relatively easily with chlorosulfonic acid (at 80-130°) to form monosulfonic acids in 34-45% yields. The compounds (II) and (III) which differ by a methyl group in the 4-position, are sulfonated with approximately equal ease. Compounds (V) and (VI), which contain only one substituent, OH or NH₂, are much more difficult to sulfonate. We only succeeded in obtaining, in very low yield (10%) a sulfonated derivative of compound (V); it did not prove possible to isolate the sulfonation product of compound (VI). Dichloromethylpyrimidine (VII) is not changed when heated with chlorosulfonic acid at 100°.

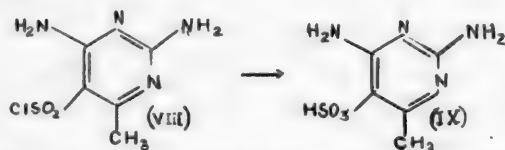
In all the five instances (I-V) monosulfonic acids were obtained. It can be confidently asserted that the sulfonic group in them occupies the 5 position. Furthermore, in compounds (I), (II), and (IV) the 5 position is the only unsubstituted position in the pyrimidine ring. The possibility of the addition of a sulfonic group to nitrogen or oxygen must be excluded; the sulfonic acids obtained were quite stable to hydrolysis; therefore it must be assumed that the SO_3H group enters the same 5 position as is entered by NO_2 and halogens.

All these sulfonic acids are white crystalline substances soluble in alkalis and water. They separate unchanged from the alkaline solutions on acidification. The sulfonic acids from (I), (II), and (III) dissolve with difficulty in cold water and have limited solubility in hot. 2,6-Diamino-4-methyl-5-sulfopyrimidine, and also 2-amino-4-methyl-5-sulfopyrimidine, are much more readily soluble in water. All the substances crystallize from water. The pyrimidine sulfonic acids are insoluble in organic solvents.

The sodium salts of the sulfonic acids from (I), (II), and (III) have better solubility in water than the sulfonic acids themselves. They all swell considerably when heated over a flame. The sodium salts have lower and sharper melting points than the corresponding sulfonic acids. 2-Amino-6-hydroxy-5-sulfopyrimidine chars on heating without melting.

As is known, the reaction of benzene derivatives with excess of chlorosulfonic acid yields the corresponding chlorosulfonates, which are isolated when the reaction mass is poured into water or ice. The pyrimidine compounds studied form sulfonic acids in analogous conditions; chlorosulfonates are not, as a rule, formed. In one instance only — in the sulfonation of 2,6-diamino-4-methylpyrimidine — a chlorosulfonate (VIII) was obtained as the initial reaction product.

To obtain this product, 2,6-diamino-4-methylpyrimidine was sulfonated at 125-130° and the reaction mass was poured over ice. The chlorosulfonate precipitate was immediately filtered off. The chlorosulfonate is readily soluble in warm water, and when the solution is cooled it crystallizes out in the pure state (m.p. 230°). The pure chlorosulfonate is gradually hydrolyzed on boiling in aqueous solution. Dilute mineral acids or alkalis rapidly hydrolyze the chlorosulfonate even in the cold; it is then converted into 2,6-diamino-4-methylpyrimidine-5-sulfonic acid (IX) (m.p. 270-272°, decomp.).



The possibility is not excluded that the sulfonation of other pyrimidine derivatives (I, II, III, V) also first results in the formation of chlorosulfonates which are rapidly hydrolyzed when the reaction mass is diluted with water. However, this question cannot be regarded as solved, especially as the literature also contains instances of chlorosulfonate formation as the result of a secondary reaction — by the action of a second molecule of chlorosulfonic acid on the sulfonic acid [5].

EXPERIMENTAL

2,6-Dihydroxy-4-methyl-5-sulfopyrimidine was described previously [4].

2-Amino-6-hydroxy-4-methyl-5-sulfopyrimidine (II). 2-Amino-6-hydroxy-4-methylpyrimidine was prepared by the condensation of guanidine carbonate with acetoacetic ester in alcohol [6].

4 g of 2-amino-6-hydroxy-4-methylpyrimidine was added in small portions with thorough stirring to 10 ml of chlorosulfonic acid heated to 110°. The reaction mixture was then held at this temperature for 15 minutes and poured into 150 g of ice; a white crystalline precipitate of the sulfonic acid separated out, and this was filtered off and thoroughly washed with water. The mother liquor was diluted with double its volume of water and left to stand. On the next day some more of the sulfonic acid was filtered off. The total yield was 2.7-2.8 g (42-44%). The sulfonic acid does not melt up to 300°, and crystallizes from water.

0.1446 g sub.: 0.1622 g BaSO_4 . 0.1122 g sub.: 0.1269 g BaSO_4 . 0.1412 g sub.: 24.4 ml N_2 (19°, 758 mm). 0.1223 g sub.: 21.2 ml N_2 (20°, 760 mm). Found %: S 15.3, 15.5; N 20.0, 20.2. $\text{C}_5\text{H}_7\text{O}_4\text{N}_3\text{S}$. Calculated %: S 15.6; N 20.4.

The sodium salt was prepared by dissolving 2.05 g of 2-amino-6-hydroxy-4-methyl-5-sulfopyrimidine in a

solution of 0.4 g NaOH in 20 ml of water. The solution was evaporated to dryness and the dry residue was recrystallized from water. M.p. 278-280°. The salt is easily soluble in water and insoluble in alcohol.

2-Amino-6-hydroxy-5-sulfopyrimidine (III). 2-Amino-6-hydroxypyrimidine was prepared by the reaction of malic acid with urea in oleum [7].

2 g of 2-amino-6-hydroxypyrimidine was added in small portions, with stirring, to 8 ml of chlorosulfonic acid at 110-115°. The reaction solution was kept at this temperature for 10-15 minutes and poured into 40 g of ice. A white crystalline precipitate of the sulfonic acid gradually separated on external cooling with ice-cold water and rubbing with a glass rod. After 2 hours the precipitate was filtered off, washed thoroughly with water and dried at 80°. Yield 0.85 g (34%). When heated on a metal plate the substance chars slowly without melting. It was purified for analysis by recrystallization from a large volume of water. It may be purified by reprecipitation with hydrochloric acid from alkaline solution.

0.1028 g sub.: 0.1254 g BaSO₄. 0.1430 g sub.: 0.1732 g BaSO₄. 0.0654 g sub.: 12.2 ml N₂ (21°, 765 mm). 0.1062 g sub.: 19.4 ml N₂ (22°, 772 mm). Found %: S 16.7, 16.5; N 21.6, 21.3. C₄H₅O₃N₃S. Calculated %: S 16.7; N 21.9.

The sodium salt was formed by the addition of 0.95 g of 2-amino-6-hydroxy-5-sulfopyrimidine to a solution of 0.2 g of NaOH in 10 ml of water. A slurry was formed, which was evaporated to dryness on a water bath. The weight of the dry residue was 1.03 g. The substance crystallizes from water, m.p. 288-290°.

2,6-Diamino-4-methyl-5-sulfopyrimidine (IV). 2,6-Diamino-4-methylpyrimidine was prepared by the action of alcoholic ammonia under pressure on 2-amino-6-chloro-4-methylpyrimidine [8].

1.6 g of 2,6-diamino-4-methylpyrimidine was added gradually, over a period of 35-40 minutes, to 7 ml of chlorosulfonic acid heated to 125°, with stirring. The reaction solution was kept at 120-130° for 10 minutes and poured into 50 g of ice. A precipitate was gradually formed. The reaction mixture was left to stand and on the following day the precipitated sulfonic acid was filtered off and washed with water. Yield 1.1-1.2 g (40-43%). It was recrystallized from water in the presence of animal charcoal, m.p. 270-272°.

0.1063 g sub.: 0.1224 g BaSO₄. 0.0992 g sub.: 0.1141 g BaSO₄. 0.1004 g sub.: 24.6 ml N₂ (23°, 760 mm). 0.1004 g sub.: 24.0 ml N₂ (21°, 766 mm). Found %: S 15.6, 15.7; N 27.9, 27.8. C₅H₇O₃N₄S. Calculated %: S 15.6; N 27.5.

2,6-Diamino-4-methylpyrimidine-5-chlorosulfonic acid. 1.6 g of 2,6-diamino-4-methylpyrimidine was added at 125-130° with stirring to 7 ml of chlorosulfonic acid over a period of 40 minutes. The reaction mixture was held 10 minutes at this temperature and then poured into a beaker with ice (50 g) cooled with ice-cold water from the outside. The yellowish precipitate of the chlorosulfonate was at once filtered off, rapidly washed with ice-cold water twice (15-20 ml water each time) and dried at 40-50°. Yield 1.0 g (36%). To purify the product it was dissolved in warm water (60-80°), a little animal charcoal was added, the solution filtered, the colorless solution cooled rapidly, and the dazzling white crystals of the chlorosulfonate separated off, m.p. 228-230°.

0.1096 g sub.: 23.2 ml N₂ (19°, 763 mm). 0.1024 g sub.: 22.1 ml N₂ (20°, 760 mm). Found %: N 24.8, 24.9. C₅H₇O₂N₄SCl. Calculated %: N 25.2.

The chlorosulfonate was hydrolyzed by boiling 0.2 g of it in 10 ml of water. After 15 minutes of boiling, traces of hydrochloric acid appeared in the solution. After 1 hour the hydrolysis was complete; the hydrochloric acid was precipitated by silver nitrate, the precipitate filtered off, and the filtrate boiled for another 30 minutes. No hydrochloric acid was detected in this solution. The solution was evaporated to dryness, and the dry residue recrystallized from water, m.p. 270°. A sample mixed with 2,6-diamino-4-methyl-5-sulfopyrimidine showed no depression of melting point.

The alkaline hydrolysis of the chlorosulfonate was carried out by dissolving a weighed portion with gentle heating in 0.1 N caustic soda solution. After 1 hour the solution was back-titrated with 0.1 N hydrochloric acid solution.

0.1226 g sub.: 10.8 ml 0.1 N. NaOH. C₅H₇O₂N₄SCl. Calculated: 11.0 ml 0.1 N NaOH.

2-Amino-4-methyl-5-sulfopyrimidine (V). 2-Amino-4-methylpyrimidine was prepared by the reduction of 2-amino-6-chloro-4-methylpyrimidine with zinc dust [9].

5 g of 2-amino-4-methylpyrimidine was added at 115° with stirring to 12 ml of chlorosulfonic acid. After

40 minutes the reaction solution was poured into 75 g of ice. The solution was then diluted with one and a half times its volume of water and left to stand. After 2 months a yellowish crystalline precipitate separated out. Yield 0.7 g (10%). The substance melts and swells when heated on a metal plate. It begins to darken at 230° and gradually decomposes. It crystallizes from water to form small shiny crystals.

0.0682 g sub.: 0.0830 g BaSO₄. 0.0821 g sub.: 0.0996 g BaSO₄. Found %: S 16.7, 16.6. C₅H₇O₃N₃S. Calculated %: S 17.0.

SUMMARY

1. The sulfonation of pyrimidine derivatives containing two substituents (OH, NH₂) in the 2,4, or 6 positions, takes place relatively easily. Monosulfonic acids with a sulfo group in the 5 position are formed. 2-Amino-6-hydroxy-4-methyl-5-sulfopyrimidine, 2-amino-6-hydroxy-5-sulfopyrimidine, and 2,6-diamino-4-methyl-5-sulfopyrimidine were prepared.

2. In the action of chlorosulfonic acid on 2,6-diamino-4-methylpyrimidine the first reaction product is 2,6-diamino-4-methylpyrimidine-5-chlorosulfonic acid, which readily passes into 2,6-diamino-4-methyl-5-sulfopyrimidine.

3. The sulfonation of pyrimidine derivatives with only one hydroxy or amino group is much more difficult. 2-Amino-4-methyl-5-sulfopyrimidine was prepared in 10% yield.

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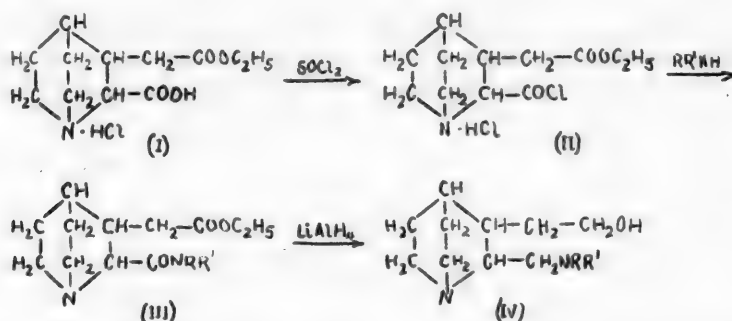
SYNTHESIS OF SUBSTITUTED 2-AMINOMETHYL-3-(β -HYDROXYETHYL)-QUINUCLIDINES

M. V. Rubtsov, E. E. Mikhlina, and V. Ya. Furshtatova

In the previous communications the synthesis of [2-carboxyquinuclidyl-(3)]-acetic acid, a number of its derivatives, and also of some substituted 2-aminomethyl-3-(β -aminoethyl)-quinuclidines was described [1, 2].

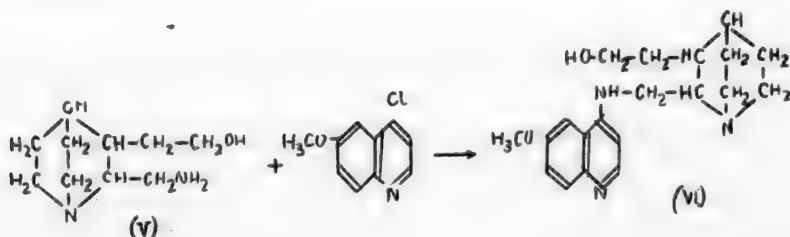
In further studies of the properties of 2,3-disubstituted quinuclidines it was found that the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid is readily hydrolyzed on standing in aqueous solution to form the acid ester. It was also found that the ethyl ester of quinuclidine-2-carboxylic acid is also easily hydrolyzed in such conditions to give quinuclidine-2-carboxylic acid. Consideration of the properties of these esters suggests that the carboethoxyl group in the 2 position of the quinuclidine nucleus is saponified in the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid, and the semi-ester formed by hydrolysis has the structure of 3-carboethoxymethylquinuclidine-2-acetic acid (I).

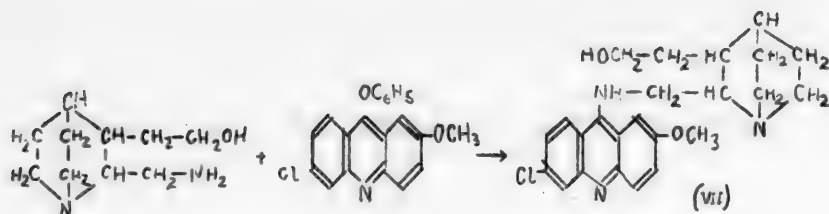
This last was used to synthesize a number of 2-alkyl(aryl)aminomethyl-3-(β -hydroxyethyl)-quinuclidines according to the scheme:



The hydrochloride of 3-carboethoxymethylquinuclidine-2-carboxylic acid (I) was converted with the aid of thionyl chloride into the acid chloride (II), which was then treated with alkyl or aryl amines. The alkyl or aryl amides of 3-carboethoxymethylquinuclidine-2-carboxylic acid (III) so formed were reduced by lithium aluminum hydride to the 2-alkyl(aryl)aminomethyl-3-(β -hydroxyethyl)-quinuclidines (IV). The following alkyl(aryl) amines were used for the synthesis of the amides (III): diethylaminoethylamine, diethylaminoisopentylamine, 2-aminopyridine, piperidine, 6-methoxy-4-aminoquinoline, and 2-methoxy-6-chloro-9-aminoacridine. However, the last two compounds could not be acylated with the acid chloride of 3-carboethoxymethylquinuclidine-2-carboxylic acid, and the corresponding amides (III) could not be prepared in this way.

Derivatives of 2-aminoethylquinuclidine containing quinoline (VI) and acridine (VII) ring systems were obtained by the reaction of 2-aminomethyl-3-(β -hydroxyethyl)-quinuclidine (V) with 6-methoxy-4-chloroquinoline and 2-methoxy-6-chloro-9-phenoxyacridine:





The reaction between (V) and 4-chloro-6-methoxyquinoline was carried out in phenol at 180-190°, and the reaction with 2-methoxy-6-chloro-9-phenoxyacridine in boiling butyl alcohol.

EXPERIMENTAL

3-Carboethoxymethylquinuclidine-2-carboxylic acid

13.4 g of the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid was dissolved in 250 ml of water and the solution was left at room temperature for 7 days. The water was then distilled off under vacuum and the residue dried by 4 additions and removals of benzene. The solid residue was dissolved on warming in 20 ml of anhydrous alcohol, the alcoholic solution was filtered to remove the turbidity, and 150 ml of anhydrous ether was added. The colorless crystals which formed were filtered off and washed with ether. The yield was 11.35 g of 3-carboethoxymethylquinuclidine-2-carboxylic acid, containing a small amount of [2-carboxyquinuclidyl-(3)]-acetic acid. To remove the latter, the precipitate was dissolved in 50 ml of dry chloroform, the solution was filtered to remove the di-acid insoluble in chloroform, and the chloroform solution was diluted with ether. 3-Carboethoxymethylquinuclidine-2-carboxylic acid separated out in the form of colorless crystals readily soluble in alcohol, chloroform, and water, and insoluble in ether. M.p. 180-182°.

4.709 mg sub.: 0.245 ml N₂ (19°, 731 mm). 7.755 mg sub.: 3.29 ml 0.01 N. H₂SO₄. Found %: N 5.85, 5.94. C₁₂H₁₉O₄N. Calculated %: N 5.81.

3-Carboethoxymethylquinuclidine-2-carboxylic acid hydrochloride was isolated from a chloroform solution of the base by means of the calculated amount of an alcoholic solution of hydrogen chloride. The substance is a white crystalline powder, readily soluble in alcohol and water, insoluble in ether, chloroform, and acetone. M.p. 228-229° (decomp.). Yield 11.85 g (85.8%).

3.498 mg sub.: 6.618 mg CO₂; 2.229 mg H₂O. 4.015 mg sub.: 7.678 mg CO₂; 2.578 mg H₂O. 9.003 mg sub.: 0.410 ml N₂ (23°, 728 mm). 8.755 mg sub.: 0.393 ml N₂ (23°, 728 mm). Found %: C 51.63, 52.18; H 7.13, 7.18; N 5.04, 4.96. C₁₂H₂₀O₄NCl. Calculated %: C 51.89; H 7.21; N 5.04.

3-Carboethoxymethylquinuclidine-2-carboxylic acid amide. 4.7 g of 3-carboethoxymethylquinuclidine-2-carboxylic acid hydrochloride and 47 ml of thionyl chloride were heated together at 60-65° for 4 hours. The precipitate dissolved completely during this time. The thionyl chloride was distilled off under vacuum, and its last traces were removed by 3-fold addition of benzene followed by its removal under vacuum. The colorless precipitate of the 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride was suspended in 50 ml of dry ether and a stream of ammonia passed into the suspension for 2 hours. The reaction mass was treated with 40 ml of 50% potash solution and extracted with chloroform. The chloroform solution was dried with potash, the chloroform was distilled off under vacuum, and the solid residue recrystallized from dry ether. The yield was 3.65 g (89.6%) of 3-carboethoxymethylquinuclidine-2-carboxylic acid amide in the form of colorless crystals easily soluble in organic solvents and in water. M. p. 102-103°.

4.168 mg sub.: 9.191 mg CO₂; 3.220 mg H₂O. 3.350 mg sub.: 7.420 mg CO₂; 2.520 mg H₂O. 5.970 mg sub.: 0.628 ml N₂ (22°, 735 mm). Found %: C 60.17, 60.26; H 8.64, 8.39; N 11.78. C₁₂H₂₀O₃N₂. Calculated %: C 60.00; H 8.33; N 11.66.

The diethylaminoethylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared as described above from 3 g of the acid hydrochloride was treated with a solution of 5.52 g of diethylaminoethylamine in 60 ml of dry ether. The yield was 2.95 g (80%) of the substance in the form of a colorless viscous liquid easily soluble in organic solvents and in water. M.p. 185-186° at 0.4 mm.

3.384 mg sub.: 7.861 mg CO₂; 2900 mg H₂O. 3.110 mg sub.: 7.239 mg CO₂; 2.793 mg H₂O. 6.375 mg sub.: 0.720 ml N₂ (22.5°, 729 mm). 9.640 mg sub.: 1.062 ml N₂ (22.5°, 734 mm). Found %: C 63.39, 63.52; H 9.58, 10.04; N 12.55, 12.35. C₁₈H₃₃O₃N₃. Calculated %: C 63.72; H 9.73; N 12.4.

The diethylaminoisopentylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 2.5 g of the acid hydrochloride was added to a solution of 4.28 g of diethylaminoisopentylamine in 30 ml of anhydrous ether. The appropriate treatment yielded 2.62 g of the amide (76.1%), b.p. 190-191° at 0.3 mm. It is a viscous greenish liquid with a strong amine odor, easily soluble in organic solvents, less easily in water.

3.911 mg sub.: 9.433 mg CO₂; 3.601 mg H₂O. 5.710 mg sub.: 0.557 ml N₂ (22°, 739 mm). Found %: C 65.82; H 10.30; N 10.98. C₂₁H₃₉O₃N₃. Calculated %: C 66.14; H 10.23; N 11.00.

The pyridyl-(2')-amide of 3-carboethoxymethylquinuclidine-2-carboxylic acid. The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 3 g of the acid chloride was treated with 6.1 g of pyridine in 40 ml of anhydrous benzene at room temperature. In fractionation of the reaction products the pyridine was first driven off under a pressure of 10 mm, and the amide was then distilled. B.p. 210-212° at 0.3 mm. It is an extremely viscous yellow liquid which crystallizes when rubbed with a rod. The crystals melt at 56-58° after being washed in petroleum ether. They are easily soluble in ether, benzene, acetone, and alcohol, and with difficulty in water. Yield 2.4 g (70.2%).

3.711 mg sub.: 8.708 mg CO₂; 2.381 mg H₂O. 3.708 mg sub.: 8.766 mg CO₂; 2.504 mg H₂O. 4.088 mg sub.: 0.494 ml N₂ (25°, 733 mm). Found %: C 64.03, 64.51; H 7.18, 7.55; N 13.34. C₁₇H₂₃O₃N₃. Calculated %: C 64.35; H 7.25; N 13.25.

N-[3-carboethoxymethylquinuclidinoyl-(2)]-piperidine

The 3-carboethoxymethylquinuclidine-2-carboxylic acid chloride hydrochloride prepared from 3 g of the acid was added to a solution of 4.5 g of piperidine in 30 ml of dry benzene. The reaction mass was heated on a water bath at 60-70° for 3 hours and then treated in the usual way. The yield was 1.95 g (50.8%) of a substance with b.p. 160-162° at 0.4 mm, m.p. 45-47°. Colorless crystals easily soluble in water and in organic solvents.

3.932 mg sub.: 9.601 mg CO₂; 3.161 mg H₂O. 3.215 mg sub.: 7.795 mg CO₂; 2.598 mg H₂O. 9.490 mg sub.: 6.02 ml 0.01 N H₂SO₄. Found %: C 66.63, 66.17; H 9.00, 9.04; N 8.88. C₁₇H₂₃O₃N₃. Calculated %: C 66.25; H 9.09; N 9.09.

2-Aminomethyl-3-(β-hydroxyethyl)-quinuclidine

2.4 g of a solution of lithium aluminum hydride in 60 ml of anhydrous ether was added to a solution of 3.65 g of carboethoxymethylquinuclidine-2-carboxylic acid amide in 80 ml of anhydrous benzene. The reaction mass was kept heated at the boil for 20 hours. The excess LiAlH₄ was then decomposed by 4 ml of water, and the precipitate was filtered off and washed with benzene. The combined solutions were dried with potash and evaporated under a vacuum; the residue was distilled. B.p. 157-160° at 0.3 mm. Yield 2.2 g (78.7%).

2-Aminomethyl-3-(β-hydroxyethyl)-quinuclidine is a colorless viscous liquid easily soluble in organic solvents. It was identified as the picrate, m.p. 202-204°.

4.352 mg sub.: 6.528 mg CO₂; 1.652 mg H₂O. 6.327 mg sub.: 1.000 ml N₂ (24°, 744 mm). Found %: C 40.94; H 4.25; N 17.78. C₁₀H₂₀ON₂ · 2C₆H₅O₇N₃. Calculated %: C 41.15; H 4.05; N 17.43.

2-Diethylaminoethylaminomethyl-3-(β-hydroxyethyl)-quinuclidine. 2.4 g of the diethylaminoethylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid was reduced by 0.82 g of lithium aluminum hydride in 65 ml of ether, as described above. The yield was 1.3 g (65%) of a viscous greenish liquid with a weak amine odor, easily soluble in organic solvents and in water. B.p. 170-172° at 0.35 mm.

8.290 mg sub.: 1.069 ml N₂ (22°, 741 mm). Found %: N 14.56. C₁₆H₃₃ON₃. Calculated %: N 14.84.

2-Diethylaminoisopentylaminomethyl-3-(β-hydroxyethyl)-quinuclidine. 3.8 g of the diethylaminoisopentylamide of 3-carboethoxymethylquinuclidine-2-carboxylic acid was reduced by 1.2 g of LiAlH₄ in 80 ml of ether. The yield was 2.8 g (86.5%) of a colorless viscous liquid, easily soluble in organic solvents and in water. B.p. 185-186° at 0.3 mm.

3.651 mg sub.: 9.390 mg CO₂; 3.912 mg H₂O. 7.445 mg sub.: 0.840 ml N₂ (23°, 749 mm). Found %: C 70.18; H 11.98; N 12.83. C₁₉H₃₉ON₃. Calculated %: C 70.16; H 12.00; N 12.91.

2-[Pyridyl-(2')-aminomethyl]-3-(β -hydroxyethyl)-quinuclidine. 4.35 g of the pyridyl-(2')-amide of 3-carboethoxymethylquinuclidine-2-carboxylic acid was reduced by 2.16 g of LiAlH_4 in a mixture of 60 ml of ether and 70 ml of benzene. The amine formed was extracted with chloroform. Evaporation of the solvent yielded 2.5 g (69.8%) of a substance with m.p. 137-139°. The compound consists of small pale yellow crystals, easily soluble in alcohol and chloroform, difficultly soluble in benzene, insoluble in ether, soluble in water upon gentle heating.

3.799 mg sub.: 9.570 mg CO_2 ; 2.950 mg H_2O . Found %: C 68.75; H 8.68. $\text{C}_{15}\text{H}_{23}\text{ON}_3$. Calculated %: C 69.00; H 8.81.

N-[3-(β -hydroxyethyl)-quinuclidineaminomethyl-(2)]-piperidine

2.35 g of N-[3-carboethoxymethylquinuclidinoyl-(2)]-piperidine was reduced by 1.2 g of LiAlH_4 in a mixture of 50 ml of ether and 50 ml of benzene. The yield was 1.3 g (67.6%) of a white crystalline powder, easily soluble in chloroform, alcohol, and acetone, difficultly soluble in cold water and easily in hot. After recrystallization from benzene the amine melts at 116-117°.

4.800 mg sub.: 12.555 mg CO_2 ; 4.765 mg H_2O . 7.366 mg sub.: 5.67 ml 0.01 N H_2SO_4 . Found %: C 71.38; H 11.11; N 10.78. $\text{C}_{15}\text{H}_{23}\text{ON}_2$. Calculated %: C 71.43; H 11.11; N 11.11.

2-[6'-Methoxyquinolyl-(4')]-aminomethyl-3-(β -hydroxyethyl)-quinuclidine

1.25 g of 2-aminomethyl-3-(β -hydroxyethyl)-quinuclidine, 1.31 g of 6-methoxy-4-chloroquinoline, and 15 g of redistilled phenol were heated together on an oil bath at 190° for 3 hours. The cooled reaction mass was poured into 50 ml of 20% caustic soda solution and extracted with chloroform. The chloroform solution was dried with potash, the chloroform was distilled off, and the remaining oily crystals were triturated with ether. The residue was filtered off, washed with a small quantity of chloroform, and then recrystallized from a mixture of chloroform and ether (1:6). The yield was 1.5 g (46.6%) of colorless crystals easily soluble in alcohol and chloroform and insoluble in ether or water. M.p. 207-209°.

7.900 mg sub.: 0.838 ml N_2 (25°, 728 mm). Found %: N 11.68. $\text{C}_{20}\text{H}_{27}\text{O}_2\text{N}_3$. Calculated %: N 12.01.

2-[(2'-Methoxy-6'-chloroacridyl-(9'))-aminomethyl]-3-(β -hydroxyethyl)-quinuclidine

0.62 g of 2-aminomethyl-3-(β -hydroxyethyl)-quinuclidine, 0.96 g of 2-methoxy-6-chloro-9-phenoxyacridine and 25 ml of n-butyl alcohol were heated together on an oil bath at 125-130° for 23 hours. The butyl alcohol was distilled off under vacuum, the residue was dissolved in 20 ml of ether, and the ether solution deposited 0.96 g of a substance after standing for 1 hour. The substance was crystallized from 20 ml of 50% alcohol. The result was bright yellow crystals, easily soluble in alcohol and chloroform, insoluble in ether or water. M.p. 165-166.5°. Yield 78.3%.

3.131 mg sub.: 7.782 mg CO_2 ; 1.820 mg H_2O . 8.080 mg sub.: 0.678 ml N_2 (23°, 756 mm). Found %: C 67.82; H 6.50; N 9.62. $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_3\text{Cl}$. Calculated %: C 67.70; H 6.58; N 9.87.

The substance was converted into the hydrochloride, which was in the form of yellow crystals easily soluble in water, difficultly in alcohol, insoluble in ether or acetone. M.p. 258-260° (decomp.).

4.099 mg sub.: 3.602 mg AgCl . Found %: Cl 21.74. $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_3\text{Cl} \cdot 2\text{HCl}$. Calculated %: Cl 21.36.

SUMMARY

Hydrolysis of the diethyl ester of [2-carboxyquinuclidyl-(3)]-acetic acid yielded 3-carboethoxymethyl-quinuclidine-2-acetic acid. This was used for the synthesis of a number of 2-alkyl(aryl)aminomethyl-3-(β -hydroxyethyl)-nuclidines.

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• T. p. = C. B. Translation pagination.

APPLICATION OF INFRARED ABSORPTION SPECTRA TO INVESTIGATION OF THE INTERMEDIATE PRODUCTS OF VITAMIN A AND CAROTENE SYNTHESIS

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The infrared spectra of certain compounds of the polyene series, prepared synthetically, were studied. Infrared spectra can provide valuable information on the structure of these compounds, and in addition investigation of the infrared spectra of the reaction products can serve as a method for determining the extent to which any given stage of the synthesis has been completed.

The absorption spectra in the infrared region were measured with a Hilger spectrometer D-209, the single-beam model being used. The source of light was a saltpeter rod heated to 1140°. The measurements were carried out in the region between 2.5 and 15 μ with the aid of a rock salt prism. Rock salt plates were used for the cells. The thickness of the layer of substance under investigation was regulated by layers of aluminum foil, and was 10, 20, 30 and 70 μ . Exact regulation of the layer thickness, however, was difficult because of the high viscosity of the substances studied.

I. The infrared spectrum of pseudoionone. Pseudoionone is a starting material for the preparation of β -ionone, which forms the basis of all known syntheses of vitamin A and carotenoids. We studied the infrared spectra of pseudoionone synthesized from methylheptenone [1] (Fig. 1a) and also of pseudoionone prepared from natural citral (Fig. 1b). Both the pseudoionones were redistilled under vacuum (0.1 mm Hg) before determination of their spectra. The spectra of the two pseudoionones coincide almost completely. The greatest interest is presented by the vibration forms of the components of the intense triplet band in the region 1675-1590 cm^{-1} . The 1675 cm^{-1} absorption band evidently corresponds to the vibration frequency of the $\text{C}=\text{O}$ carbonyl group conjugated with two double carbon-carbon bonds, as a result of which it is much lower than the vibration frequency of the carbonyl group in aliphatic ketones, 1720 cm^{-1} [2]. Because of conjugation, the frequency of the $\text{C}=\text{O}$ double bond is similarly lowered; this corresponds to the absorption band in the 1590 cm^{-1} region, while the isolated double bond at the end of the chain corresponds to the absorption band at 1635 cm^{-1} .

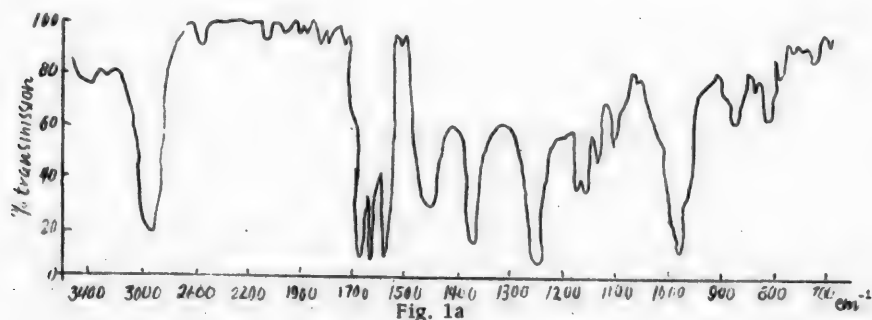
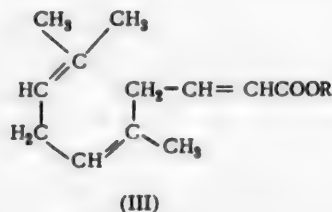
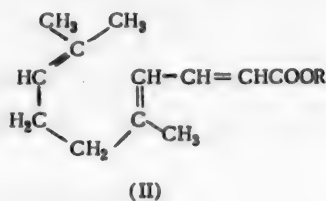
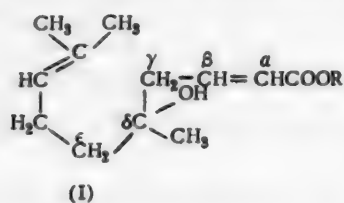


Fig. 1a

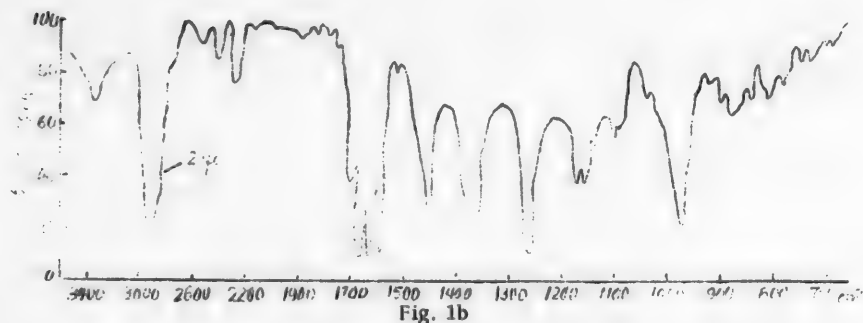
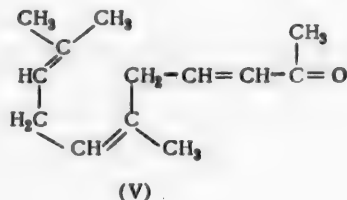
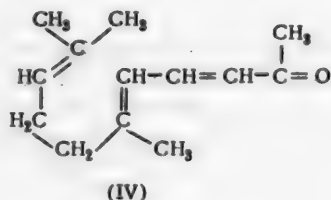
Thus, the spectra of synthetic pseudoionone support the view that its structure is correctly described by the generally accepted formula. There are, however, some differences between the spectra of the pseudoionones obtained from different starting materials.

1. The 1700 cm^{-1} absorption band is found only in the spectrum of pseudoionone synthesized from methylheptenone. This band corresponds to the vibration frequency of the carbonyl bond, somewhat lower than the $\text{C}=\text{O}$ vibration frequency in ketones of the aliphatic series. Its presence in the spectrum of the pseudoionone can only be explained by the presence of admixtures of substances the molecules of which do not have such strong conjugation of the carbon-carbon double bonds as exists in pseudoionone, where the $\text{C}=\text{O}$ bond is conjugated with a chain consisting of two conjugated carbon-carbon bonds. It must be remembered that in the synthesis of pseudoionone from methylheptenone by condensation of the latter with γ -bromocrotonic ester, a hydroxy ester (I) is obtained, which can split

off water to give isomers with the double bond in the $\gamma\delta$ and $\delta\epsilon$ positions (II) and (III):



and consequently the pseudoionone which is formed later can also be obtained in two isomeric forms, $\gamma\delta$ (IV) and $\delta\epsilon$ (V):



In the $\delta\epsilon$ (V) isomer, conjugation of the C=C bonds is disrupted, and therefore their effect on the CO group is rather weaker than in the $\gamma\delta$ (IV) isomer, and the vibration frequency of the C=O group will be decreased less by the influence of one C=C bond conjugated with it. Thus, in the molecule of 2-methylbutene-1-one-3 the C=O group is conjugated with only one C=C group, and in the spectrum of this substance [3] the C=O group is represented by an absorption band at 1700 cm^{-1} , in just the region in which an absorption band is found in the spectrum of pseudoionone synthesized from methylheptenone.

Evidently, the main mass of the pseudoionone formed in the synthesis is the $\gamma\delta$ -isomer, as is shown by the presence in its spectrum of a very intense band at 1675 cm^{-1} , which corresponds to a C=O group conjugated with two C=C bonds, and only a small percentage of the $\delta\epsilon$ -isomer is obtained, as the corresponding C=O band at 1700 cm^{-1} in the spectrum of synthetic pseudoionone has low intensity.

2. The absorption band at 882 cm^{-1} in the spectrum of pseudoionone synthesized from methylheptenone is more intense than the 815 cm^{-1} band, while these two bands have the same intensity in the spectrum of pseudoionone synthesized from natural citral. Absorption bands in the 880 cm^{-1} region are characteristic of cis-isomers [4]. We

may therefore conclude that pseudoionone synthesized from methylheptenone contains more *cis*-isomer than the pseudoionone synthesized from natural citral.

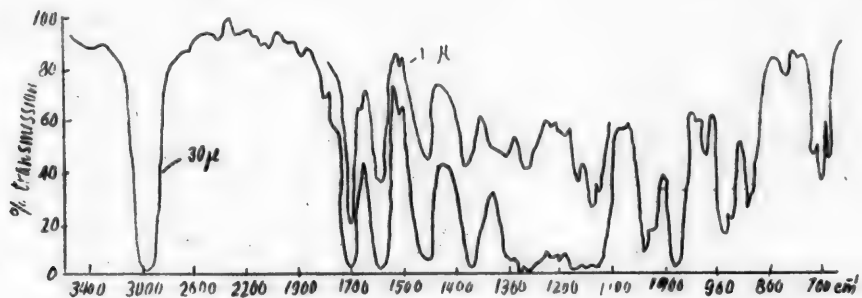


Fig. 2.

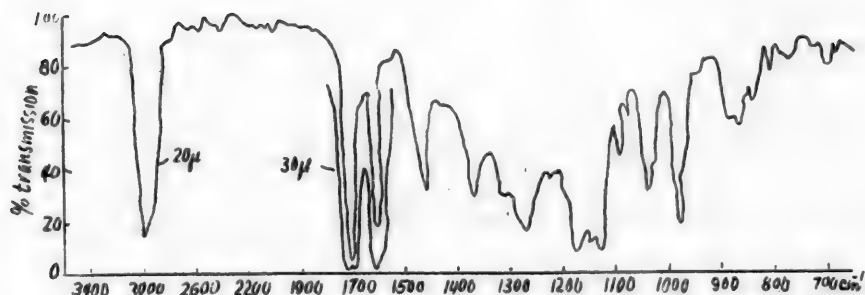


Fig. 3.

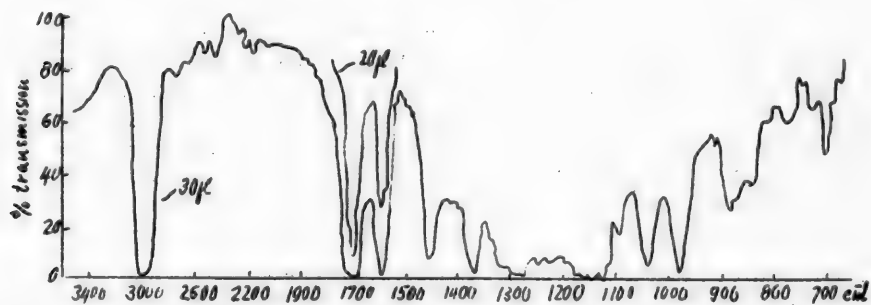


Fig. 4.

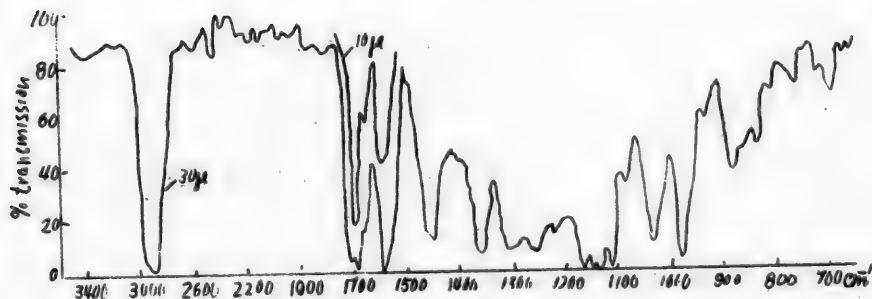


Fig. 5.

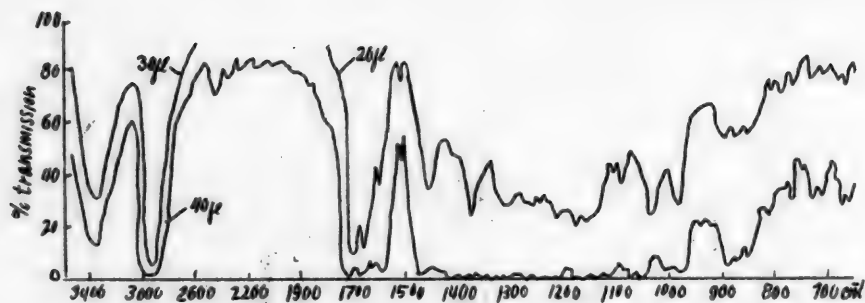


Fig. 6.

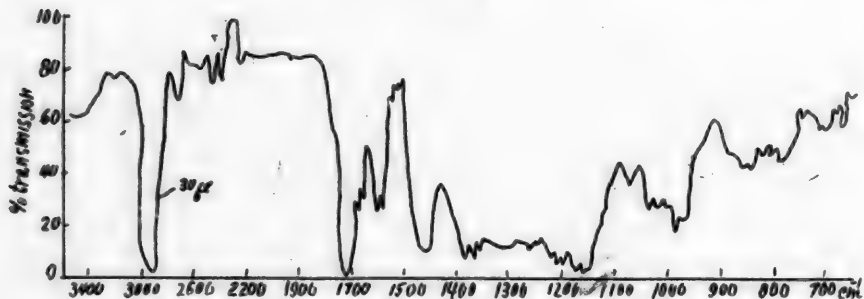
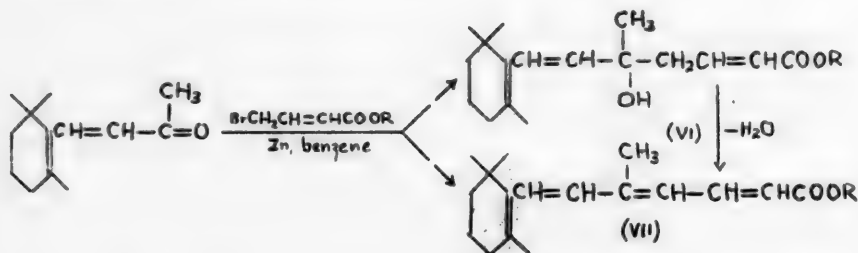


Fig. 7.

3. A fairly considerable difference between the spectra of the pseudoionones is found in the 3400 cm^{-1} region. In this region the absorption band in the spectrum of pseudoionone synthesized from methylheptenone is approximately 3 times as intense as the one in the spectrum of pseudoionone synthesized from natural citral. This region contains the absorption bands of OH groups linked by hydrogen bonds. The presence of traces of moisture, which might cause absorption in the region, is improbable as both the pseudoionones were dried and distilled under vacuum before the spectra were measured. The appearance of these bands in the spectra of the pseudoionones can be attributed only to the partial enolization of the pseudoionones, and evidently the reaction conditions (alkaline medium at the last stage of the synthesis) favor a greater shift of the keto-enol equilibrium in the direction of the enol form in pseudoionone obtained from methylheptenone. It is also possible that the predominance of the *cis*-isomer in this pseudoionone favors its enolization in some way.

II. The infrared spectrum of the methyl ester of β ionolidenecrotonic acid. The methyl ester of β -ionolidenecrotonic acid was obtained by the condensation of β -ionone with the methyl ester of γ -bromocrotonic acid in the presence of activated zinc:



The main reaction product was the methyl ester of β -ionolidenecrotonic acid (VII). In addition, the reaction mixture contained unchanged β -ionone.

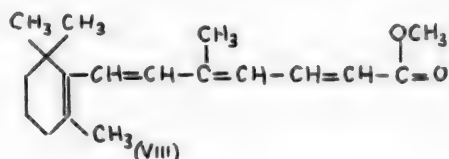
Most workers report the yield of crystalline β -ionolidenecrotonic acid by this reaction as 7.5-10% of theoretical. Evidently, the yield is greatly decreased by side reactions. The great similarity between the properties of the

reaction products indicates the formation of a number of isomeric compounds.

Separation of the reaction products and their identification by chemical methods presents considerable difficulties. By investigating the infrared spectra of the reaction products we attempted to determine the mechanism of the reaction and to clarify the nature of the side reactions.

The reaction products were first subjected to chromatographic separation with the aid of aluminum oxide column, and this was followed by the measurement of the infrared spectra of 4 consecutive chromatographic fractions. In addition, the spectrum of the product formed by the action of diazomethane on an ether solution of the acids obtained from the easily saponified fraction of the original ester was measured. The standard comparison sample of the methyl ester of β -ionolidenecrotonic acid was prepared by the action of diazomethane on the pure crystalline acid of m.p. 156-157.5°.

The spectrum of the ester (Fig. 2) proves the validity of formula (VIII):



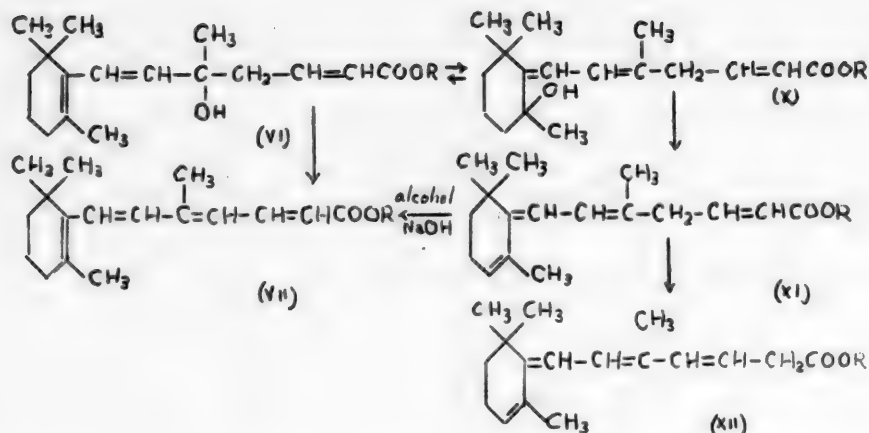
In fact, the 1700 cm^{-1} band corresponds to the $\text{C}=\text{O}$ carbonyl group in the ester grouping. In comparison with esters of the aliphatic series [2] the value of the vibration frequency for $\text{C}=\text{O}$ is decreased by 45 cm^{-1} due to conjugation of the carbonyl group with the polyene chain. The vibration frequency of the $\text{C}=\text{C}$ linkage at 1600 cm^{-1} in the polyene chain is also decreased as the result of conjugation. The ester grouping $\text{C}-\text{O}-\text{CH}_3$ corresponds to the 1270 , 1200 , and 1170 cm^{-1} bands, which are characteristic for methyl esters of acids with long carbon atom chains [5]; the 1270 cm^{-1} band corresponds mainly to vibration of the $\text{C}-\text{O}$ bond in the ester group, while the 1200 and 1170 cm^{-1} bands correspond to deformational vibration of the whole ester group. The 1140 cm^{-1} band also evidently owes its appearance in the spectrum to one of the vibrational forms of the ester group, as it is found in the spectra of many esters [3].

In addition, an examination of the spectrum leads to the conclusion that the $\text{C}-\text{O}-$ linkage is conjugated with the polyene chain, as the spectrum of the ester studied contains bands at 1040 and 1020 cm^{-1} , which are found in the spectra of unsaturated acids and esters in which conjugation between $\text{C}-\text{O}-$ and $\text{C}=\text{C}$ bonds exists, and are not found in the spectra of acids and esters where there is no such conjugation.

The presence of a cyclohexene ring in the ester molecule is proved by the existence of bands in the 1130 , 1450 , and 1650 cm^{-1} regions [3] in its spectrum. The 1650 cm^{-1} band is masked by the 1700 and 1600 cm^{-1} bands. With a thinner layer of the ester under investigation it appears as a small shoulder on the right-hand slope of the 1700 cm^{-1} absorption band.

The spectrum of the 1st fraction (Fig. 3) obtained by chromatography from technical ethyl ester of β -ionolidenecrotonic acid shows certain changes when compared with the spectrum of the standard ester. The broad intense absorption band in the 1700 cm^{-1} region has two maxima at 1700 and 1720 cm^{-1} . Two absorption bands are probably superposed here. The band in the 1700 cm^{-1} region, as has already been stated, corresponds to the vibration frequency of the carbonyl group in the ethyl ester of β -ionolidenecrotonic acid, lowered considerably (by 45 cm^{-1}) by the effect of conjugation with the long polyene chain. The position of the second maximum in the 1720 cm^{-1} region indicates that the 1st fraction contains substances similar to ethyl crotonate, in which the carbonyl group is conjugated with a smaller number of double bonds than in the ester of β -ionolidenecrotonic acid, and therefore its vibration frequency is not lowered so much (by 25 cm^{-1} instead of 45 cm^{-1}). In fact, the $\text{C}=\text{O}$ group absorption band in the spectrum of ethyl crotonate lies in this region [3]. This view is also supported by the shift of the maximum of the 1610 cm^{-1} band into the region of higher frequencies relative to the standard ester (1610 cm^{-1}), which indicates a shortening of the chain of conjugated double carbon-carbon bonds.

The observed shifts of the bands corresponding to the vibrations of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups into the higher frequency regions may be considered in the light of allyl and prototropic regroupings which accompany dehydration:



In the ester (XI), which is isomeric with the β -ionolidenecrotonic ester, and which is formed as a side product, the C=O group is conjugated with only one C=C double bond, as in the crotonic ester. The chain of conjugated C=C bonds in the ester (XI) is shorter than this chain in the ester (VIII). The yield of the β -ionolidenecrotonic ester is partly decreased owing to allyl regroupings. The hypothesis that allyl regroupings accompany the reaction by which the β -ionolidenecrotonic ester is formed, which we put forward as the result of a study of the infrared spectra of the reaction products, was also proposed by a number of workers who studied analogous reactions [6].

The spectra of the 2nd and 3rd fractions (Fig. 4 and 5) are very similar to the spectrum of the 1st fraction, and all that has been said about the 1st fraction applies to them also.

The spectrum of the 4th fraction (Fig. 6) differs very significantly from the spectrum of the pure ester. Firstly, the spectrum of the 4th fraction contains a very intense broad band in the 3380 cm^{-1} region which is characteristic of compounds with hydroxyl groups associated by means of hydrogen bonds. The presence of bands characteristic of the cyclohexene ring in the spectrum of this fraction, together with the hydroxyl group band, indicates the presence of residues of the non-hydrated hydroxy ester (VI). This view is apparently contradicted by the position of the carbonyl group absorption band in the 1700 cm^{-1} region, which is 20 cm^{-1} below its position in the spectrum of ethyl crotonate (1720 cm^{-1}), where the C=O group is conjugated with one C=C group, as in the case of the hydroxy ester (VI). However, this may be explained by the supposition that the carbonyl groups of one molecule are joined by hydrogen bonds to hydroxyl groups of another, and the vibration frequency of these groups is lowered due to the hydrogen bond.

In the spectrum of the substance obtained by the action of diazomethane on an ether solution of the acids synthesized from the easily saponifiable portion of the original ester the carbonyl group band lies in the 1730 cm^{-1} region. This indicates that the carbonyl group is not conjugated with the polyene chain, the presence of which in the molecules of this substance is shown by the $1600\text{--}1585 \text{ cm}^{-1}$ absorption band.

Such compounds of the type (XII) may be formed as the result of allyl and prototropic regroupings which accompany dehydration under the action of alkaline agents.

The general similarity between the spectra of the substances studied shows the presence of a mixture of compounds with the same structural elements but differing in the positions of the latter and in the degree of double bond conjugation. The results indicate the formation of structural isomers of β -ionolidenecrotonic acid during condensation of β -ionone with esters of γ -bromocrotonic acid in the presence of zinc, by the Reformatsky reaction.

SUMMARY

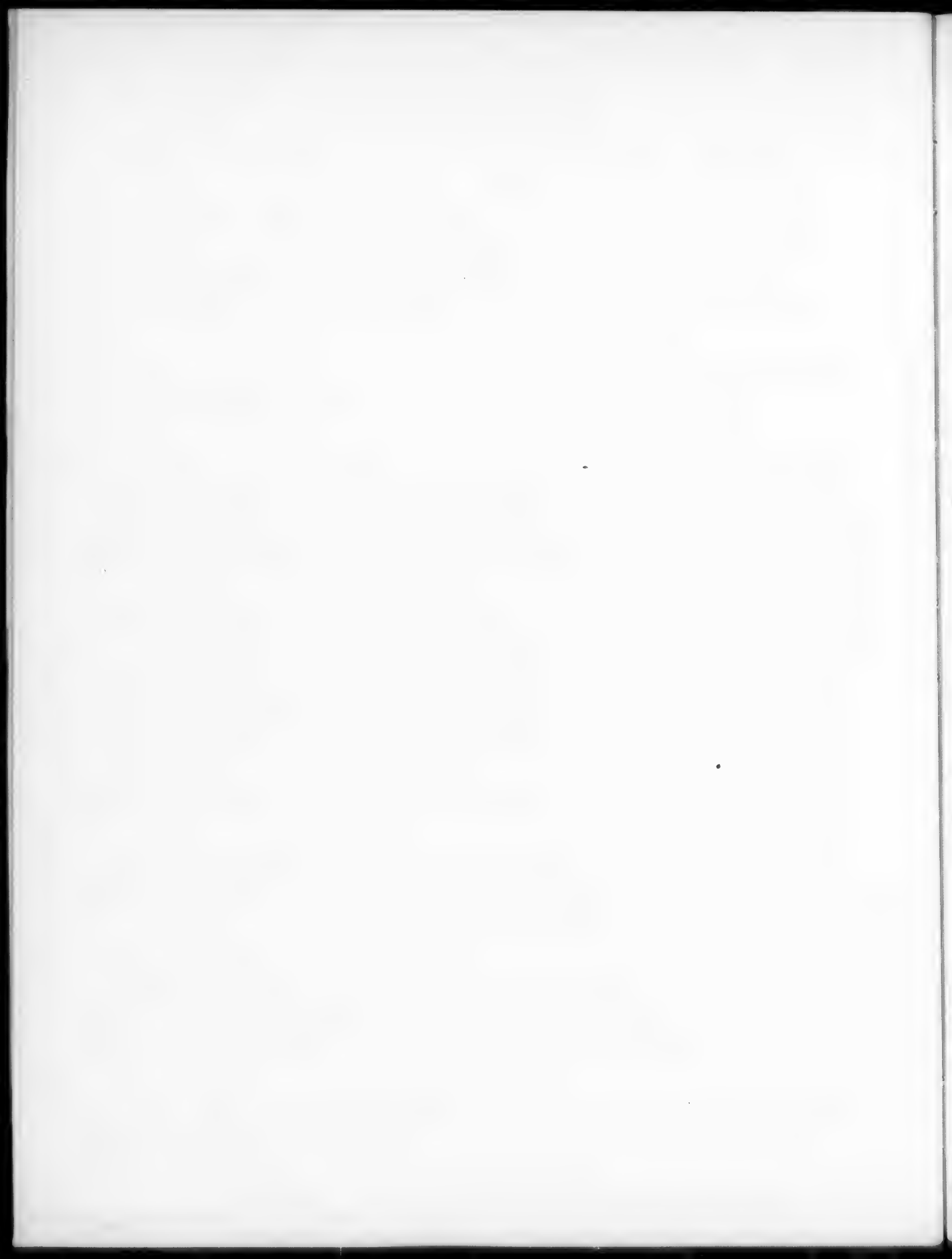
A study was made of the infrared spectra of pseudoionones synthesized from methylheptenone and from natural citral, and also of the methyl ester of β -ionolidenecrotonic acid and four consecutive fractions obtained by its chromatographic purification.

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THE MICROSTRUCTURE OF PROTEINS

XIII. THE BEHAVIOR OF DIACETYLDIKETOPIPERAZINE IN ITS REACTIONS WITH AMINES

R. G. Petrova, L. N. Akimova, and N. I. Gavrilov

The reaction of diacetyldiketopiperazine with amines was first described by Bergmann, when it was shown that when amines act on acetylated diketopiperazine [1], and also on acetylated histidine [2], theobromine [2], and other amides [3], acetyl or benzoyl groups pass from the amides to the amines. A similar transformation was observed by Bergmann by the action of arginine base in alcohol on diacetyldiketopiperazine [1]. The transacetylation was accompanied by decomposition of diacetyldiketopiperazine with the formation, first, of N,N'-diacetylglycylglycine, which was then converted into N-acetylglycylglycine by the removal of an acetyl group from nitrogen. In Bergmann's view, acyl-substituted amides, such as diacetyldiketopiperazine, are capable of acylating compounds with free or substituted amino groups. A similar process was also observed by Bergmann in the case of acylated ketoheteroamide rings. Even prior to Bergmann's work in 1924-1927, Brunner [4] studied the transformations of diacyl amides by the action of various amines. However, in these researches, in contrast to those of Bergmann, the intermediate reaction products were isolated and shown to be amidines. The results of these researches prompted us to repeat the experiments of Brunner and Bergmann with diacetyldiketopiperazine which, according to Brunner, should lead to the formation of an amidine. Such experiments were carried out by the present authors [5] with diacetyldiketopiperazine and esters of amino acids (glycine, tyrosine); a careful study of the reaction products showed convincingly that the reaction proceeds in two directions, noted by Bergmann and earlier by Brunner. Thus, in addition to the transacetylation reaction, the formation of an acetylated amidine was shown. Later the mechanism of this reaction was established and its possible directions in accordance with the medium chosen indicated. Simultaneously Prokofyev [6] found yet a third direction for this reaction; in a study of the reaction between diacetyl and dichloroacetyldiketopiperazines with aminopyrimidine in an aqueous medium, symmetrical bis-2,5-pyrimidylpiperazine amidine was isolated. The reaction was accompanied by formation of acetic acid.

Thus, research on the acetyl derivatives of diketopiperazine revealed not only the nature of the final products of their reactions with amines, but also the mechanism of the reaction itself. In all these cases diacetyldiketopiperazine reacted symmetrically.

From our studies of the reactions of diacetyldiketopiperazine it is possible to indicate a number of directions which depend not only on the structure of the substance used, but on the reaction conditions (medium, temperature). Three types of diacetyldiketopiperazine reactions are recognized. The first type is the formation of exoacyl amidines (of glycine, tyrosine, benzylamine). The reaction proceeds irrespective of the presence of any particular acyl group (sulfotoluene, sulfobenzyl, phthalylglycyl, N-chloroacetyl, N-acetyl). The second type is the Bergmann transformation which leads to 1) formation of diketopiperazine and an acetyl amino acid, 2) decomposition of diacetyldiketopiperazine to form an N,N'-acetyl dipeptide, 3) formation of an amidine with the removal of an acetyl group (observed by Brunner). The third reaction type includes the formation of monoacetyldiketopiperazine, described in the present paper, which occurs in two cases: 1) by the action of amines on diacetyldiketopiperazine in certain conditions, 2) by the action of diketopiperazine on diacetyldiketopiperazine (on heating in alcohol).

In the great majority of cases these reactions proceed at room temperature in a variety of solvents. However, sometimes it is possible to detect external physical conditions which direct the reaction. For example, when benzylamine reacts with diacetyldiketopiperazine with the reaction mixture cooled by carbon dioxide, an amidine is formed. If the reaction is carried out at room temperature in benzene, chloroform, alcohol, or ether, monoacetyldiketopiperazine and the acetyl dipeptide ester are formed. The reaction between diacetyldiketopiperazine and diaminopyrimidine proceeds at room temperature, and is accompanied by evolution of heat and an almost quantitative amidine yield with acetic acid split off. Thus the direction of this reaction depends on the most varied conditions. The most interesting is the formation of exoacyl amidines by regrouping. The preparation of monoacyl diketopiperazine derivatives is not described in the literature. The formation of monoacetyldiketopiperazine in our experiments is easily explained by a Bergmann regrouping which proceeds asymmetrically. The existence of the

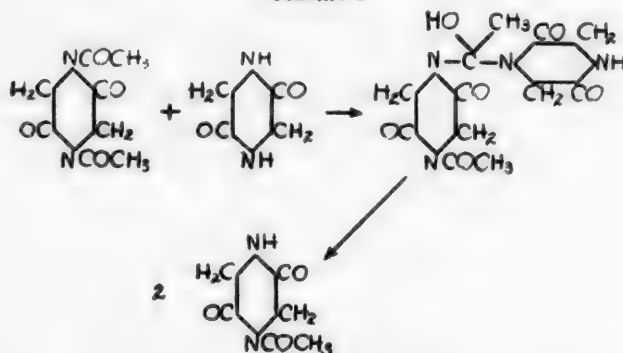
monoacetyldiketopiperazine was proved by its conversion into diacetyldiketopiperazine by the action of acetic anhydride, and its ease of decomposition by the action of acids or alkalis into the N-acetyl dipeptide ester.

The mechanism of the action of amines and amino acids on diacetyldiketopiperazine was discovered in a series of our researches. It is also confirmed by Brunner's work, who was the first to show the addition of the amino group at the amide carbonyl with the formation of an amidine, and the subsequent isomerization of the endoacyl amidines into exoacyl amidines. However, the formation both of an acetylated secondary amine, and of monoacetyldiketopiperazine by the action of diacetyldiketopiperazine on diketopiperazine shows that the addition both of amines and of diketopiperazine may take place at the carbonyl group of the endoacetyl, and acetyl amines may be formed without preliminary isomerization to exoacyl amidines.

In previous papers [5] it was shown that the reaction of diacetyldiketopiperazine with glycine esters (methyl and ethyl) produces a substance which, according to our earlier views, was the carboxylic amidine of glycine (with free carboxyl groups). Both with the use of the methyl and of the ethyl ester of glycine the composition of the substance formed was the same. This compound, which had not been described previously, was identified by analysis and study of its behavior on alcoholysis and esterification. However, the empirical formula of this compound is the same as that of monoacetyldiketopiperazine. The melting point and other properties of monoacetyldiketopiperazine, studied by us later, also proved identical with those previously reported for the carboxylic amidine.

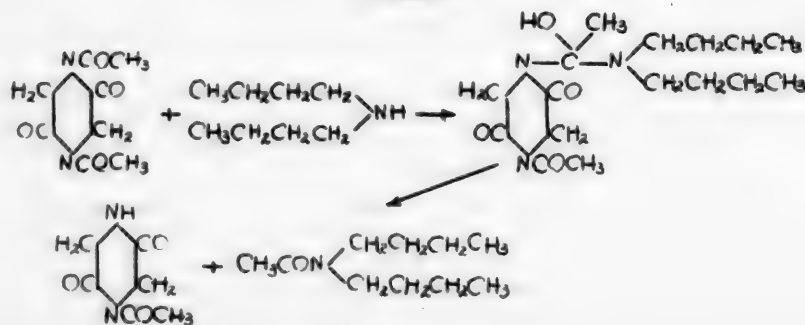
There are no methods available for the synthesis of monoacetyldiketopiperazine. Our attempts to prepare it by heating diketopiperazine with 10 times its amount of glacial acetic acid for 3 hours, with 1 and with 2 moles of acetic anhydride in 10 moles of glacial acetic acid for 11 hours and 3 days respectively, were not successful. It was observed that monoacetyldiketopiperazine is formed by the recrystallization of a mixture of diacetyldiketopiperazine and diketopiperazine from alcohol, and we assumed that these substances react in alcohol. The reaction takes place at the carbonyl in the acetyl group of diacetyldiketopiperazine and the imino nitrogen of diketopiperazine. The exoamidine formed decomposes with the formation of monoacetyldiketopiperazine according to the scheme:

Scheme 1



This scheme applies both to the Brunner reaction and to our experiments on the reaction between diacetyldiketopiperazine and a secondary amine, dibutylamine. In the latter case a regrouping of the acetyl group from the endo to the exo position is impossible, and therefore the formation of dibutylacetamide could take place direct at the exocarbonyl of the acetyl group in diacetyldiketopiperazine, as in the case of diketopiperazine.

Scheme 2



EXPERIMENTAL

I. Reactions of diacetyldiketopiperazine which proceed with the formation of monoacetyldiketopiperazine

1. With glycine ethyl ester. 2.1 g of glycine ethyl ester in 60 ml of anhydrous ether was added to 2.0 g diacetyldiketopiperazine and the mixture shaken mechanically for several hours. The precipitate was filtered off, washed with ether, and treated with acetone in the cold. The small undissolved portion of the precipitate was diketopiperazine. The acetone filtrate after evaporation under vacuum yielded monoacetyldiketopiperazine; m.p. 180°.

Found %: N 17.92. $C_8H_{10}O_3N_2$. Calculated %: N 17.95.

The ether mother liquor yielded aceturic ester; m.p. 48°. Literature data: m.p. 48° [7].

The reaction with glycine methyl ester is analogous. Monoacetyldiketopiperazine is also formed if the reaction is carried out in benzene.

2. With propylamine. 1.64 g (2 moles) of propylamine was added to 1.98 g (1 mole) of diacetyldiketopiperazine in 100 ml of anhydrous ether and the mixture cooled with snow. The mixture was shaken, and a copious precipitate was instantly formed. After 15 minutes the precipitate was filtered off, washed with ether, and treated with methyl acetate in the cold. The filtrate was concentrated under vacuum to a small volume. The substance formed gave a strong anhydride reaction, and proved to be monoacetyldiketopiperazine (m.p. 180°).

Found %: N 18.03. $C_8H_{10}O_3N_2$. Calculated %: N 17.95.

The ether filtrate was concentrated under vacuum. The oily residue was distilled, and the 223-225° fraction, which was acetylpropylamine, was collected. Literature data: b.p. 222-225° [8].

3. With aniline. a) A mixture of 2 g (1 mole) of diacetyldiketopiperazine, 100 ml of anhydrous ether, and 1.88 g (2 moles) of aniline was stirred mechanically for 3 days. The precipitate was filtered off, washed with ether, and treated with chloroform in the cold; the filtrate was evaporated under vacuum, and the precipitate formed was recrystallized from alcohol; m.p. 181-182°. Weight 1.5 g. The substance gave the anhydride reaction in the cold, and proved to be monoacetyldiketopiperazine. Total nitrogen content was 17.93%. Acetanilide, m.p. 114°, was isolated from the ether filtrate. Literature data: m.p. 115° [9].

b) 5 g (1 mole) of diacetyldiketopiperazine was dissolved with heating in 100 ml of benzene, and 4.7 g (2 moles) of aniline was added to the cooled solution. The solution was left to stand for twenty-four hours, and the precipitate was filtered off and washed with benzene and ether. The monoacetyldiketopiperazine (m.p. 176-178°) melted at 180-181° after recrystallization from alcohol.

Found %: N 18.13. $C_8H_{10}O_3N_2$. Calculated %: N 17.95.

Concentration of the benzene filtrate under vacuum gave acetanilide; m.p. 115°.

4. With benzylamine. A mixture of 1.8 g (1 mole) of diacetyldiketopiperazine, 90 ml of anhydrous ether, and 2 ml (2 moles) of benzylamine was mechanically stirred for 30 minutes at room temperature. The precipitate was filtered off, washed with ether, and treated with acetone in the cold; monoacetyldiketopiperazine was isolated from the filtrate. Yield 1.4 g (98%).

Found %: C 46.10, 46.24; H 5.09, 5.10; N 18.09. $C_8H_{10}O_3N_2$. Calculated %: C 46.15; H 5.12; N 17.95.

Acetylbenzylamine was isolated from the ether filtrate; m.p. 60°. Literature data: m.p. 60-61° [10].

Found %: N 9.43. $C_9H_{11}ON$. Calculated %: N 9.39.

With 1 mole of benzylamine the yield of monoacetyldiketopiperazine was 95%.

5. With dibutylamine. A mixture of 2 g (1 mole) of diacetyldiketopiperazine, 50 ml of ether, and 2.6 g (2 moles) of dibutylamine was shaken mechanically at room temperature for 30 minutes. The precipitate was filtered off, washed with ether and recrystallized from anhydrous alcohol. Monoacetyldiketopiperazine was obtained; m.p. 181°. Yield 1.5 g (94%). Total nitrogen 17.89%. The ether filtrate was evaporated under vacuum and the oily residue was distilled, the 244-245° fraction, which was acetyldibutylamine, being collected. Literature data: b.p. 243-245° [10]. The reaction in benzene took a similar course.

The formation of monoacetyldiketopiperazine in this reaction suggests the formation of an intermediate

compound at one of the acetyl groups in diketopiperazine (Scheme 2). This Scheme is confirmed by the reaction between diacetyldiketopiperazine and diketopiperazine, when monoacetyldiketopiperazine was again formed.

6. With diketopiperazine. 4 g of diacetyldiketopiperazine (1 mole) and 2.3 g of diketopiperazine (1 mole) in 40 ml of alcohol were boiled together for 3 hours. The precipitate was filtered off, washed with alcohol, and recrystallized from hot alcohol after filtering off the unreacted diketopiperazine. M.p. 181°. Analysis showed it to be monoacetyldiketopiperazine.

7. With β -naphthylamine. A mixture of 2 g of diacetyldiketopiperazine, 2.9 g of β -naphthylamine, and 50 ml of anhydrous ether was stirred mechanically for 3 days at room temperature and then warmed for several hours on the water bath. The precipitate was filtered off, washed repeatedly with ether, and dried in a vacuum; m.p. 179°. The total nitrogen (17.77%) shows the substance to be monoacetyldiketopiperazine. Unreacted β -naphthylamine was removed from the ether filtrate by precipitation with petroleum ether; m.p. 112°; acetyl- β -naphthylamine m.p. 132°. Literature data: m.p. 132° [11].

8. With p-nitroaniline. A mixture of 2 g of diacetyldiketopiperazine, 1.78 g of p-nitroaniline, and 50 ml of anhydrous ether was shaken mechanically for 3 days and then heated for 5 days. There was no reaction, and only the starting substances were isolated.

II. Reactions of diacetyldiketopiperazine which proceed with the formation of acetyl-glycylglycine ester

1. With benzylamine. 4.3 g of benzylamine was added to 4 g of diacetyldiketopiperazine in 125 ml of alcohol, and the mixture was shaken 3-5 minutes till the precipitate dissolved. After standing for 30 minutes at room temperature the precipitate was filtered off. The product was monoacetyldiketopiperazine; m.p. 180°. The alcoholic filtrate was concentrated under vacuum, and ether was added to the residue. The precipitate formed was filtered off and washed with ether; m.p. 150°. The substance obtained was the ethyl ester of acetylglycylglycine. Mol.wt. 219 (Rast's method). Literature data: m.p. 153° [12].

Found %: N 14.09. $C_8H_{14}O_4N_2$. Calculated %: N 13.86.

The ethyl ester of acetylglycylglycine was converted into acetylglycylglycine by saponification of the ester groups with alkali.

0.0716 g sub.: consumed 3.67 ml 0.1 N NaOH. $C_8H_{14}O_4N_2$. Calculated: 3.52 ml 0.1 N NaOH.

Concentration of the ether filtrate in vacuum followed by addition of ligroine gave acetylbenzylamine: m.p. 60°. Literature data: m.p. 60-61°.

2. With dibutylamine. A mixture of 2 g of diacetyldiketopiperazine, 50 ml of anhydrous ethyl alcohol, and 2.6 g of dibutylamine was shaken for 2-3 minutes till the precipitate dissolved. When the alcoholic solution was concentrated under vacuum a precipitate was formed, which was filtered off and treated with chloroform in the cold. The melting point of the substance obtained from chloroform was 150-151°; mol. wt. 220 (Rast's method). Melting point of the ethyl ester of acetylglycylglycine according to the literature is 153° [12].

III. Reactions of diacetyldiketopiperazine which proceed with the formation of diketopiperazine

1. With hydrazine in alcohol. Upon the addition of 0.8 g (2 moles) of hydrazine to an alcoholic solution containing 2 g (1 mole) of diacetyldiketopiperazine, much heat was evolved and diketopiperazine was precipitated quantitatively. The medium was neutral at the end of the reaction. The weight of the diketopiperazine formed was 1.0 g, the theoretical yield. Acetyl hydrazide was isolated from the alcoholic filtrate by concentration; m.p. 66-67°. Literature data: m.p. 67° [13].

2. With hydrazine in ether. 0.8 g of hydrazine was added to 2 g of diacetyldiketopiperazine in dry ether with vigorous cooling and shaking. The precipitate formed was filtered off after 30 minutes. By its melting point and analytical data the substance was identified as diketopiperazine.

Found %: N 24.38. $C_4H_8N_2O_2$. Calculated %: N 24.56.

Concentration of the filtrate yielded acetyl hydrazide. Thus, diacetyldiketopiperazine reacts with hydrazine both in alcohol and in ether to form diketopiperazine and acetyl hydrazide.

3. Upon fusion with glycine. 1 g of diacetyldiketopiperazine (1 mole) was mixed with 0.76 g (2 moles) of

glycine in a mortar. The mixture was heated in a test tube in a glycerol bath at 125-130° for 30 minutes. The colored reaction mass was treated with hot acetone and then with alcohol. The residue, by its melting point and properties, was diketopiperazine. A small amount of unreacted diacetyldiketopiperazine was isolated from the acetone filtrate. Aceturic acid, m.p. 206°, was isolated from the alcoholic filtrate.

IV. Some reactions of monoacetyldiketopiperazine

1. Hydrolysis in the presence of alkali. 0.5 g of monoacetyldiketopiperazine in 50 ml of anhydrous alcohol was mixed with 1.5 ml of 0.1 N alcoholic alkali, and the mixture stirred mechanically for several hours. The alcoholic solution was concentrated in a vacuum, and the resultant precipitate proved to be the ethyl ester of acetylglycylglycine; m.p. 153°. The melting point of a synthesized sample of acetylglycylglycine ethyl ester was 153°. A mixture gave no melting point depression. Literature data: m.p. 153°.

2. Alcoholysis in the presence of amines. a) Benzylamine. 1.1 g of monoacetyldiketopiperazine, 0.75 ml of benzylamine, and 75 ml of anhydrous alcohol were mechanically shaken for about one hour. The slight precipitate of diketopiperazine was filtered off. Vacuum concentration of the alcoholic solution gave the ethyl ester of acetylglycylglycine; m.p. 151°.

b) Dibutylamine. 1.1 g of dibutylamine was added to 1.3 g of monoacetyldiketopiperazine in 100 ml of anhydrous alcohol. After 2-3 minutes the solution became clear. The alcoholic solution was concentrated in vacuum and the precipitate washed in ether; m.p. 149°. After recrystallization from alcohol, m.p. 152°. A mixture with acetylglycylglycine ethyl ester obtained in the previous experiment gave no melting point depression.

c) Aniline. A mixture of 0.5 g of monoacetyldiketopiperazine, 0.3 g of aniline, and 35 ml of anhydrous ethyl alcohol was stirred for several days. However, there was no reaction, and the original monoacetyldiketopiperazine was isolated.

3. Alcoholysis in the presence of hydrogen chloride. 0.5 g of monoacetyldiketopiperazine (A) in 20 ml of anhydrous alcohol saturated with HCl (titration of 1 ml of the alcohol took 1 ml of 0.1 N NaOH) was heated for about 5 minutes till the precipitate dissolved completely. Upon further heating a new substance was precipitated, the amount of which increased as the heating proceeded. In crystalline form and melting point the substance was identical with diketopiperazine. The amino nitrogen was determined by Sørensen's method after hydrolysis with water and heating on the water bath for 3 and 30 hours. Diketopiperazine (B) was simultaneously hydrolyzed in the same conditions.

Determination of amino nitrogen by Sørensen's method

Heating for 3 hours: (A) 0.2150 g sub. : took 0.45 ml of 0.2 N NaOH (5.86%). (B) 0.2121 g sub. : took 0.15 ml of 0.2 N NaOH (1.98%). Heating for 30 hours: (A) 0.2219 g sub. : took 0.58 ml of 0.2 N NaOH (7.32%). (B) 0.2195 g sub. : took 0.14 ml of 0.2 N NaOH (1.8%).

The alcoholic filtrate was evaporated in vacuum to a small volume, and ether was added. The precipitate was filtered off, washed with ether, and dried; m.p. 182°. The substance gave the ninhydrin and biuret reactions of the dipeptide type. The reaction for halogens was positive. The substance was the hydrochloride of glycylglycine ethyl ester. Literature data: m.p. 182°.

Found %: N 13.99. $C_6H_{13}O_3N_2Cl$. Calculated %: N 14.2.

Therefore the acid hydrolysis of monoacetyldiketopiperazine yields diketopiperazine and the hydrochloride of glycylglycine ethyl ester.

4. Acetylation to diacetyldiketopiperazine. The action of heat on monoacetyldiketopiperazine with 5 times the quantity of acetic anhydride resulted in the formation of diacetyldiketopiperazine. The yield was theoretical. M.p. 102°. Literature data: m.p. 102°. The formation of diacetyldiketopiperazine is a proof, though indirect, of the structure of monoacetyldiketopiperazine. For complete clarification of the structure of monoacetyldiketopiperazine experiments on the action of acids and alkalis on it in alcoholic solutions were carried out. Acid hydrolysis with 0.1 N hydrochloric acid in anhydrous alcohol produced diketopiperazine and the hydrochloride of glycylglycine ethyl ester.

Under the action of alcoholic alkali (1.5 ml of 0.1 NaOH in 50 ml of alcohol) the diketopiperazine ring was opened with the formation of acetylglycylglycine ethyl ester. This esterification in the presence of alkali is a peculiar and interesting phenomenon. Monoacetyldiketopiperazine is decomposed similarly by the action of benzylamine and butylamine in alcohol.

SUMMARY

Another direction — the formation of monoacetyldiketopiperazine — is added to the numerous directions in the reactions between diacetyldiketopiperazine and amine derivatives. Of the most interesting reactions one should be noted, which leads either to splitting off of acetylamine or to the decomposition of diacetyldiketopiperazine by the action of acids and alkalis to form the acetyl dipeptide. The formation of monoacetyldiketopiperazine is in agreement with the properties of some diketopiperazine derivatives. As is known, diketopiperazine and its derivatives have a tendency to a whole series of asymmetric reactions which lead either to asymmetric rupture of the diketopiperazine ring or to unequal activity of the acyl-substituted groups.

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THE ALKALOIDS OF ACONITUM TALASSICUM M. POP.

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The paper on the alkaloids of Aconitum soongoricum [1] already drew attention to the great theoretical and practical interest presented by study of the group of alkaloids of the genus Aconitum.

The roots of Aconitum talassicum M. Pop. (local name, "kara-parpi") have long been used by the peoples of Central Asia as a medical remedy for a number of diseases. They were first collected for chemical investigation in 1937 in the Talas-Alatau mountains (Western Tyan-Shan). In view of the rarity of this plant its collection involved great difficulties. The first batch of plants collected were used by Konovalova and Orekhov [2] (with the participation of S. Yunusov, who gathered the plants) to isolate the total alkaloids, which comprised 1.64% of the dry plant weight. About one-third of the total was resolved by complex methods, and four new alkaloids were isolated. The following empirical and constitutional formulas were established for them:

Talatisine	$C_{20}H_{29}O_3N$ or $C_{19}H_{23}(NCH_3)(OH)_3 F_1$.
Talatisamine	$C_{22}H_{35}O_4N$ or $C_{19}H_{24}(NH(OH)(OCH_3)_3)$.
Isotalatisidine	$C_{23}H_{37}O_5N$ or $C_{19}H_{23}(NC_2H_5)(OH)_3(OCH_3)_2$.
Talatisidine	

The above formulas show that the new alkaloids are of the atizine type, that is, they contain fewer substituent groups than the high molecular aconitines, and therefore form a convenient basis for an approach to the hypothetical nucleus of the aconitic alkaloids, $C_{19}H_{28}NH$.

In 1949 a new extensive growing area of the Talassic aconite was discovered in the Kul-say region (the Turkestan range). The relatively simple formulas of the bases contained in this plant, the availability of the raw material, and certain considerations of the variability of alkaloids with conditions of growth [3], led us to return to an investigation of the alkaloids of this plant.

Most of the raw material studied was gathered either in the budding stage, or in the flowering and post-fertilization stages. The alkaloid content during these stages of the plant development was fairly high: 1.01% in the shoots and 1.92% in the roots.

Separation of the alkaloid mixture by use of the different solubilities in organic solvents, and also by fractionation by basicity function, resulted in the isolation of only about 20% (of the total weight) of the crystalline alkaloids. It was observed, however, that further quantities of the bases crystallized out of the solutions after prolonged standing.

On the assumption that the remaining alkaloids are present as esters which may be largely amorphous, the total amount of alkaloids was subjected to saponification. This immediately raised the yield of crystalline bases to 50%, and the acid saponification products contained veratric acid. Both alkalies and acids were used for the saponification; the reaction products and the yields of crystalline alkaloids were identical in both cases.

The alkaloid present in greatest amount has m.p. 145-146° and does not rotate the plane of polarization. A mixture with the talatisamine isolated by Konovalova and Orekhov showed no melting point depression. Detailed study of this alkaloid showed that its formulas (empirical and constitutional) do not agree with the findings of these authors.

The results of elementary analysis, iodine determination in the hydriodide, and determination of molecular weight by titration, carried out again, corresponded most closely to the formula $C_{24}H_{39}O_5N$ (instead of $C_{22}H_{35}O_4N$).

According to Konovalova and Orekhov, talatizamine contains, in addition to three methoxyl groups, secondary nitrogen and one hydroxyl group. We showed that talatisamine forms a methiodide with methyl iodide, and splits off acetaldehyde on oxidation with permanganate. These reactions show that the nitrogen in the alkaloid is tertiary

and is joined to an ethyl radical. The talatisamine molecule, in fact, contains 3 methoxyl groups and 2 active hydrogen atoms, but both the latter belong to hydroxyl groups, as talatisamine forms both a mono and a diacetyl derivative, both with very definite basic properties.

Therefore the constitutional formula of talatisamine may be written as follows:



The second alkaloid, with m.p. 246-247° and $[\alpha]_D + 36.5^\circ$, which contains one double bond and no methoxyl groups, is apparently talatisine. The elementary analysis data are in good agreement with the empirical formula $C_{26}H_{29}O_3N$ which was proposed by Konovalova and Orekhov [2].

EXPERIMENTAL

22.9 kg of the dried and powdered plant material (leaves and stems) was wetted with 10% ammonia solution, loaded into a percolator, and exhaustively extracted with dichloroethane (6 times). The dichloroethane solution was shaken first with 10% and then with 5% sulfuric acid till the alkaloids were completely extracted. The previously filtered solution was made alkaline with a concentrated solution of ammonia in the cold; the alkaloid mixture was precipitated as a viscous mass which was separated from the solution by decantation. The ammoniacal mother liquor was saturated with salt and repeatedly extracted with chloroform. The chloroform extract was concentrated to a small volume and poured into a basin. After complete evaporation of the solvent 51.0 g of a dark brown amorphous mass remained.

a) Treatment of the sparingly soluble alkaloids. 180 g of the pale brown, not quite dry mass was dissolved in 460 ml of 10% sulfuric acid, and the solution was heated under a reflux condenser on a boiling water bath for 5 hours. The acid solution was cooled and shaken several times with ether (ether solution A), filtered to remove resins and slime, and made alkaline with ammonia. The precipitated alkaloids were extracted with chloroform. The chloroform solution was evaporated to a small volume. The resinous mass, after complete removal of the solvent in a vacuum, was triturated with methyl alcohol; a white finely crystalline precipitate of talatisamine was formed (71.2 g), m.p. 140-142°. The methanol liquor was evaporated to dryness and, after the addition of a few milliliters of water, was treated with ligroine, ether, and chloroform. The solutions were evaporated to a small volume and allowed to stand, when an additional amount of talatisamine crystals was formed: 16.0 g from the ligroine solution, 2.9 g from ether, and 2.0 g from chloroform. The total yield of talatisamine was thus 92.1 g. The ether solution A on evaporation deposited white, easily sublimed needles, m.p. 177-179°. These were easily soluble in ether, alcohol, acetone, alkalies, ammonia, and insoluble in water or acids. When recrystallized from dilute alcohol the needles melted at 180-181°. The analytical results showed convincingly that they were veratric acid, $C_8H_8(OCH_3)_2COOH$.

Found %: C 58.97, 59.10; H 5.55, 5.78; OCH_3 33.11, 33.50; equiv. 180.14, 179.36. $C_9H_{10}O_4$. Calculated %: C 59.33; H 5.47; $2OCH_3$ 34.07; equiv. 182.17.

b) Treatment of the alkaloids extracted from the mother liquor. 51.0 g of the mixture of bases was dissolved in 200 ml of 10% sulfuric acid. The filtered solution was separated into 5 fractions according to basicity strength by consecutive precipitation with calculated amounts of ammonia. The final mother liquor was exhaustively extracted with chloroform. The chloroform solution was evaporated to dryness in a vacuum (6th fraction). Each fraction, consisting of a colored amorphous mass, was dissolved in methyl alcohol. Upon standing, the 1st fraction deposited 1.30 g of crystals with m.p. 249-253° (substance was not investigated); 0.66 g of a mixture of alkaloids (m.p. 210-225°) crystallized from the 3rd fraction; the 4th fraction deposited 1.07 g of talatisine, m.p. 245-246°; the 5th fraction deposited 0.67 g of talatisamine, m.p. 144-145°; the 2nd fraction did not yield any crystals.

The alcoholic mother liquors from the 3rd and 4th fractions were combined and partially evaporated to yield a further 2.1 g of talatisamine, m.p. 143-145°, and also 8.8 g of a mixture of talatisine and talatisamine (m.p. 140-180°). It proved possible to separate this mixture by means of 30 ml of cold benzene: the insoluble portion of the mixture (3.0 g) was pure talatisine; the benzene solution, after evaporation to a small volume, deposited 5.2 g of talatisamine.

The alcoholic mother liquors (after separation of the crystals) and the non-crystallizing alcoholic solutions of the 2nd and 6th fractions were combined and saponified by 10% alcoholic KOH solutions for 5 hours. A methanol solution of the saponified alkaloids was evaporated (if possible to remove the alcohol completely) and treated first with ligroine and then with ether.

The ligroine extract was exhaustively extracted with 10% sulfuric acid. The acid solution was made alkaline

with 25% ammonia solution, and the alkaloids were consecutively extracted with gasoline and ether. When the ligroine solution was concentrated, 2.5 g of talatisamine crystallized out, and the ether solution yielded 0.28 g of a mixture of alkaloids (m.p. 210-220°).

An ether extract of the saponified alkaloids yielded 0.5 g of talatisamine on evaporation. The residue, after saponification with the alkaloids which did not dissolve in ether and ligroine, was dissolved in sulfuric acid. The acid solution was filtered out, made alkaline with ammonia, and the alkaloids again extracted with ether at the moment of separation. Concentration of the ether solution yielded 0.45 g of a mixture of alkaloids (m.p. 210-225°).

Thus, the mother liquor yielded 10.97 g of talatisamine, 4.07 g of talatisine, and 1.39 g of mixed alkaloids. In the aggregate, 231.0 g of the mixture gave 103.07 g of talatisamine, 4.07 g of talatisine, and 2.69 g of a mixture of alkaloids which was not investigated. The total yield of the crystalline portion relative to the whole mass was 47.6%.

In the same way a total amount of 1250 g of alkaloids was extracted from 65 kg of roots, and separation gave 498 g of talatisamine, 21.7 g of talatisine, and 12.3 g of an unresolved crystalline mixture of alkaloids (m.p. 210-225°).

Talatisamine. The crude talatisamine was crystallized several times from methanol until crystals with constant m.p. 145-146° were obtained.

4.720, 3.251 mg sub.: 11.767, 8.136 mg CO₂; 3.968, 2.761 mg H₂O. 7.125, 5.675 mg sub.: 0.225, 0.186 ml N₂ (22°, 734 mm). 10.530, 8.988 mg sub.: 8.81, 7.63 ml 0.05 N. Na₂S₂O₃ (for OCH₃). 3.154 mg sub.: 3.30 ml 0.02 N Na₂S₂O₃ (for NC₂H₅). 0.9909, 1.0036 g sub.: 23.536, 23.785 ml 0.1 N H₂SO₄ (methyl red). Found %: C 68.04, 68.29; H 9.41, 9.50; N 3.53, 3.66; OCH₃ 21.64, 21.95; NC₂H₅ 15.01; equiv. 421.11. C₂₄H₃₉O₅N. Calculated %: C 68.37; H 9.33; N 3.32; 3OCH₃ 22.08; NC₂H₅ 10.21; equiv. 421.56.

Talatisamine hydrobromide was prepared by the addition of hydrobromic acid to the base till an acid reaction was obtained. The liquid was left in an open basin for several days, when crystals were formed which had m.p. 78-80° after recrystallization from ethyl acetate. Talatisamine hydrobromide crystallizes with two molecules of water. After drying in a vacuum the melting point of the salt was almost unchanged (80-81°).

Found %: H₂O 7.15. C₂₄H₃₉O₅N · HBr · 2H₂O. Calculated %: H₂O 6.70.

Talatisamine hydriodide. 3 g of the base was dissolved in 30 ml of acetone with gentle heating. The clear solution was cooled, and concentrated hydriodic acid was added (till weakly acid to litmus), followed by the careful addition of 25 ml of ether. After several days crystals of the hydriodide were obtained in the form of warty nodules, m.p. 66-68°. Yield 3.8 g. Talatisamine hydriodide is easily soluble in water and alcohol, less so in acetone. After recrystallization from a mixture of alcohol and acetone (1:1) the salt was precipitated in the form of colorless four-sided prisms with 3 molecules of water of crystallization; m.p. 67.5-68.5°.

0.6010 g sub. in 10.0 ml water: $\alpha_D - 0.77^\circ$, $[\alpha]_D - 12.8^\circ$.

1.6962 g sub.: 0.1481 g H₂O. 0.2034, 0.1911 g sub.: 3.30, 3.16 ml 0.1 N AgNO₃. Found %: H₂O 8.73; I 20.57, 20.96. C₂₄H₃₉O₅N · HI · 3H₂O. Calculated %: H₂O 8.95; I 21.03.

The anhydrous salt has no sharp melting point: it shrinks at 130° and then froths.

0.5472 g sub. in 10 ml water: $\alpha_D - 0.77^\circ$, $[\alpha]_D - 14.8^\circ$.

0.2520, 0.2532 g sub.: 4.64, 4.61 ml 0.1 N AgNO₃. Found %: I 23.39, 23.12. C₂₄H₃₉O₅N · HI. Calculated %: I 23.09.

Monoacetyltalatisamine. A mixture of 1 g of the base and 2 ml of acetic anhydride was placed in a flask with a ground glass stopper and left to stand for 13 days till a viscous homogeneous mass was formed. A small amount of water was added to this mass, the solution was made alkaline with ammonia, and the precipitated base was extracted with ether. The oil obtained by evaporation of the ether solution crystallized after standing. After recrystallization from methanol the monoacetyltalatisamine had m.p. 97-98°. Saponification of the acetyl derivative gave the original talatisamine.

Diacetyltalatisamine. A mixture of 1 g of the base and 2 ml of acetyl chloride was left in a closed vessel till a homogeneous solution was formed. After 12 days the excess acetyl chloride was driven off from the reaction mass (first on the water bath; then under vacuum). A small amount of water was added to the residue, the solution was made alkaline with ammonia, and the precipitated base was exhaustively extracted with ether. The ether extract

was concentrated to a small volume and poured into a basin. After complete volatilization of the solvent an oil remained, which crystallized after standing. The diacetyltalatisamine was recrystallized from methyl alcohol and had m.p. 127-129°. A sample mixed with monoacetyltalatisamine showed depression of melting point.

0.5540 g sub. in 10.0 ml methyl alcohol: $\underline{1}$ 10.0, $\alpha_D - 0.25^\circ$, $[\alpha]_D - 5.05^\circ$.

0.5136, 0.4945 g sub.: 10.1, 9.75 ml 0.1 N HCl (methyl red). Found %: equiv. 508.5, 507.2. $C_{28}H_{49}O_7N$. Calculated: equiv. 505.63.

Saponification of diacetyltalatisamine. Alcoholic alkali solution was added to weighed samples of diacetyltalatisamine. The mixture was boiled on the water bath under a reflux condenser and the excess alkali was titrated with acid.

0.3182, 0.3016 g sub.: 11.86 11.86 ml 1 N KOH. Found %: CH_3CO 11.30, 11.90. $C_{24}H_{37}N(CH_3COO)_2$. Calculated %: CH_3CO 11.60.

After removal of the solvent on the water bath and then under vacuum, alkali was added to the solution, and the base was extracted with ether. Crystals were deposited from the ether solution after evaporation, and after recrystallization from methanol the crystals melted at 144-145°. No melting point depression was given by a sample mixed with talatisamine.

Talatisamine methiodide. A mixture of 4 g of the base and 10 ml of methyl iodide was sealed in an ampoule and heated on a boiling water bath for 6 hours. The ampoule was opened and the crystals formed were separated off and washed with ether, m.p. 220-221°. Yield 1.35 g. Crystals of the original talatisamine were deposited from the mother liquor after evaporation. The melting point of the methiodide did not change after recrystallization from methyl alcohol with the addition of ether.

Oxidation of talatisamine. 0.5 g of potassium permanganate dissolved in 10 ml of water was added to a solution of 1 g of the base in 10 ml of N sulfuric acid cooled by ice, dropwise with stirring during 1 hour. The reaction mixture was filtered, the precipitate was washed with 6 ml of water, and the filtrate was distilled into a cooled receiver. 30 ml of hot 1% aqueous dimedon solution was added to the distillate, and the mixture was then heated for 10 minutes on the water bath. After 1 hour a bulky crystalline precipitate (0.21 g) was deposited from the cooled solution, m.p. 134-136°. After recrystallization from ligroine the crystals had m.p. 136-138°. A mixture of the condensation product of acetaldehyde with dimedon with m.p. 138-140°, melted at 138-139°.

Talatisine. Talatisine was recrystallized from methanol. The result was a colorless crystalline substance, m.p. 246-247°. Upon catalytic hydrogenation over platinum oxide the alkaloid absorbed a quantity of hydrogen which approximately corresponded to the presence of one double bond.

0.1700 g sub. in 10 ml anhydrous alcohol: $\underline{1}$ 10.0, $\alpha_D + 0.62^\circ$, $[\alpha]_D + 36.5^\circ$.

Found %: C 72.30, 72.05; H 8.72, 8.82; N 4.22, 4.47. $C_{29}H_{29}O_3N$. Calculated %: C 72.50; H 8.76; N 4.23.

SUMMARY

1. The alkaloids talatisamine and talatisine were isolated from Aconitum talassicum M. Pop. Veratric acid was found in the saponification products of the alkaloid mixture.
2. The following corrected constitutional formula is given for talatisamine as the result of functional group determinations and the preparation of certain new derivatives:



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THE ACONITE ALKALOIDS

VI. ELATINE

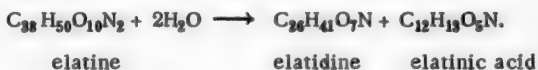
M. S. Rabinovich

The previous paper [1] gave the results of a chemical investigation of a Delphinium species — Delphinium elatum (tall larkspur) which grows in the Altay region. In addition to a new crystalline alkaloid, named eldeline, we isolated another crystalline base, provisionally designated as Base No. 2. Its peculiarity is the solubility of its sulfate in chloroform, which made it possible to isolate it in the pure state for the first time. Base No. 2 is separated from the ether mother-liquors after removal of eldeline, and its content does not exceed 0.03-0.04% of the dry plant weight. The alkaloid, recrystallized from ethyl or methyl alcohol, melts at 222-225°, specific rotation + 3.4° (in chloroform), forms an amorphous hydrochloride, m.p. 180-210° (decomp.), and a crystalline perchlorate, m.p. 175-200°. From elementary analysis data for the base and the perchlorate, the composition of the base was established as $C_{38}H_{50}O_{10}N_2$. As the newly isolated base differs in its properties from the known alkaloids, we gave it the name of elatine.

Saponification of elatine with alcoholic caustic soda solution gives a crystalline amino alcohol and a crystalline nitrogen-containing acid, which were named elatidine and elatinic acid respectively.

Elatidine, recrystallized from aqueous acetone, melts at 172-174°, and forms a crystalline hydrobromide with m.p. 206.5-207.5° (decomp.). The action of methyl iodide, as in the case of the amino alcohol delartine [2] forms the hydriodide, m.p. 197-197.5°. Acetylation of elatidine gave a monoacetyl derivative isolated as the hydrochloride, m.p. 205-208° (decomp.). On the basis of elementary analysis of the base, its hydrobromide, and the monoacetyl derivative, elatine was assigned the composition $C_{38}H_{41}O_7N$.

Elatinic acid melts at 154-155.5°, and is a dibasic acid, the equivalent of which is 125. Its composition, by elementary analysis, was established as $C_{12}H_{13}O_5N$. Thus, the alkaline hydrolysis of elatine may be represented by:



When elatinic acid is heated with 10% hydrochloric acid, two crystalline acids are formed: one of these after sublimation and recrystallization from water melted at 144-145° and was anthranilic acid. The second acid, after recrystallization from a mixture of alcohol and acetone, melted at 183-185° (decomp.), and was sparingly soluble in ether and easily in water. In its composition and properties of the decomposition products elatinic acid greatly resembles delartinic acid, which was isolated after the saponification of delartine [2]; their identity is quite probable, and this may be proved by direct comparison.

EXPERIMENTAL

Isolation of elatine

The ether mother liquor after separation of eldeline [1] was treated with 10% sulfuric acid. The resultant sulfuric acid solution was repeatedly extracted with chloroform, when the elatine passed into chloroform solution. After removal of the chloroform under vacuum a syrupy substance remained, which was dissolved in a small amount of 10% sulfuric acid. The acid solution was washed with ether, and then carefully, with cooling, made alkaline with 25% ammonia; elatine crystallized out in the form of a yellowish-grey powder. After 2 recrystallizations from ethyl alcohol (1:10) in the presence of carbon, elatine separated out as colorless needles, m.p. 222-225° in a yield of 0.03-0.04% on the dry plant weight.

0.1036 g sub. (3 ml chloroform, $\frac{1}{1}$ 0.5); $[\alpha]_D + 3.4^\circ$.

4.539 mg sub.: 10.922 mg CO₂; 3.023 mg H₂O. 3.383 mg sub.: 8.149 mg CO₂; 2.200 mg H₂O. 6.272 mg sub.: 0.244 ml N₂ (22.5°, 733.5 mm). 6.800 mg sub.: 0.259 ml N₂ (25°, 733.0 mm). 0.1035 g sub.: 1.5 ml 0.1 N HCl (methyl red). Found %: C 65.67, 65.73; H 7.45, 7.27; N 4.34, 4.20. M 690. C₃₅H₅₀O₁₀N₂. Calculated %: C 65.70; H 7.20; N 4.03. M 694.

The hydrochloride was formed upon acidification of a solution of elatine in anhydrous alcohol with alcoholic hydrochloric acid; it was isolated as an amorphous powder by the addition of anhydrous ether, and it decomposes at 180-210°.

The perchlorate was formed by mixing aqueous solutions of elatine hydrochloride and sodium perchlorate. After recrystallization from aqueous alcohol, with slow cooling, the salt with an indistinct m.p. 175-200° (decomp.) crystallized out.

3.573 mg sub.: 7.475 mg CO₂; 2.303 mg H₂O. 3.300 mg sub.: 6.842 mg CO₂; 2.074 mg H₂O. 7.051 mg sub.: 0.199 ml N₂ (23°, 735 mm). 7.165 mg sub.: 1.505 mg AgCl. 7.161 mg sub.: 1.462 mg AgCl. Found %: C 57.09, 56.58; H 7.21, 7.03; N 3.15, 3.25; Cl 5.12, 5.05. C₃₅H₅₀O₁₀N₂·HClO₄. Calculated %: C 57.42; H 6.3; N 3.52; Cl 4.47.

Elatidine

A mixture of 3 g of elatine, 10 ml of 96% alcohol, and 12 ml of 1 N NaOH was heated on the water bath under a reflux condenser for 3 hours, after which the alcohol was evaporated off. Several milliliters of water was added to the residue, and elatidine then crystallized out, the yield being 1.9 g, m.p. 160-162°. It crystallized in the form of needles after being dissolved in 1% hydrochloric acid followed by treatment with charcoal and careful neutralization of the acid solution with 2% ammonia. After recrystallization from acetone the m.p. was 172-174°.

3.855 mg sub.: 9.204 mg CO₂; 2.970 mg H₂O. 3.492 mg sub.: 8.359 mg CO₂; 2.762 mg H₂O. 8.805 mg sub.: 0.242 ml N₂ (26.5°, 730 mm). 8.610 mg sub.: 0.240 ml N₂ (26.5°, 730 mm). 4.274 mg sub.: 10.73 ml 0.02 N Na₂S₂O₃. 4.744 mg sub.: 12.00 ml 0.02 N Na₂S₂O₃. Found %: C 65.15, 65.32; H 8.62, 8.85; N 3.01, 3.05; OCH₃ 25.97, 26.15. C₃₅H₄₁O₇N. Calculated %: C 65.10; H 8.56; N 2.92; 4OCH₃ 25.88.

The hydrobromide crystallized after the addition of concentrated hydrobromic acid to a solution of elatidine in acetone. After recrystallization from acetone (1:3) and drying at 100°, m.p. was 206.5-207.5°.

3.450 ml sub.: 6.933 mg CO₂; 2.260 mg H₂O. 3.539 mg sub.: 7.088 mg CO₂; 2.371 mg H₂O. 8.420 mg sub.: 0.206 ml N₂ (27°, 730 mm). Found %: C 54.84, 54.66; H 7.33, 7.49; N 2.67. C₂₆H₄₁O₇N·HBr·0.5H₂O. Calculated %: C 54.83; H 7.55; N 2.46.

The hydriodide. 0.5 g of elatidine in methyl alcohol solution was heated with methyl iodide in a sealed tube at 70-75° for 3 hours. After evaporation of the solvent the residue was repeatedly treated with ether and then dissolved in acetone, from which it was crystallized out by the addition of anhydrous ether. After being dried to constant weight it melted at 197-198.5°. When a few drops of 5% ammonia were added to an aqueous solution of the substance, a base crystallized out which was identical with the original elatidine.

Acetylation of elatidine. A mixture of 0.5 g of elatidine and 3 ml of acetyl chloride was heated in a sealed tube at 50-60° for 16 hours. After the removal of excess acetyl chloride the residue was treated with a few milliliters of water, made alkaline with 25% ammonia, and extracted with ether. After evaporation of the solvent the remaining oily base was dissolved in acetone and converted into the hydrochloride by the addition of alcoholic hydrochloric acid. After recrystallization from alcohol-acetone mixture and the addition of anhydrous ether, acetyl-elatidine hydrochloride separated out, m.p. 205-208° (decomp.).

3.727 mg sub.: 8.238 mg CO₂; 2.779 mg H₂O. 3.900 mg sub.: 8.580 mg CO₂; 2.800 mg H₂O. 9.957 mg sub.: 0.236 ml N₂ (22°, 733 mm). 10.390 mg sub.: 0.258 ml N₂ (20.5°, 728 mm). Found %: C 60.32, 60.04; H 8.34, 8.03; N 2.65, 2.76. C₂₈H₄₃O₈N·HCl. Calculated %: C 60.26; H 7.71; N 2.51.

Elatinic acid

Acidification of the alkaline mother liquor, after isolation of elatidine, with sulfuric acid resulted in the separation of elatinic acid in the form of an oil which was converted into a pale orange powder by rubbing. This was dissolved in 1 N NaOH and then carefully acidified with 1 N hydrochloric acid; an oil was first formed, which was filtered off; the filtrate yielded a colorless crystalline acid, m.p. 154-155°.

3.133 mg sub.: 6.587 mg CO₂; 1.359 mg H₂O. 1.308 mg sub.: 2.756 mg CO₂; 0.669 mg H₂O. 7.035 mg sub.: 0.326 ml N₂ (22.5°, 733.5 mm). 7.010 mg sub.: 0.341 ml N₂ (25°, 733.0 mm). Found %: C 57.38, 57.39; H 5.49, 5.72; N 5.17, 5.37. C₁₂H₁₉O₅N. Calculated %: C 57.37; H 5.17; N 5.4.

Saponification of elatinic acid. a) 0.5 g of elatinic acid was boiled 1.5 hours with 3 ml of 10% hydrochloric acid. After dilution with an equal volume of water the solution was repeatedly extracted with ether, which was evaporated off to give 0.35 g of a crystalline acid. The acid was purified by vacuum sublimation at 120-125° followed by recrystallization from water, m.p. 141-142°. A sample mixed with anthranilic acid gave no depression of melting point.

b) The aqueous acid mother liquor, from which the anthranilic acid was extracted with ether, was evaporated under vacuum. The residue was a dark crystalline acid, in a yield of 0.15 g, which was purified by solution in a mixture of alcohol and acetone, from which it was crystallized by the addition of ether, m.p. 183-185° (without decomp.).

SUMMARY

1. From Delphinium elatum (tall larkspur) a new crystalline alkaloid with the composition $C_{30}H_{50}O_{10}N_2$, named elatine, has been isolated.
2. Elatine was found to be an ester, the alkaline hydrolysis of which gave a crystalline amino alcohol of the composition $C_{26}H_{41}O_7N$, named elatidine, and a crystalline acid of the composition $C_{12}H_{13}O_5N$, named elatinic acid.
3. The acid hydrolysis of elatinic acid gave two crystalline acids, one of which was anthranilic acid.

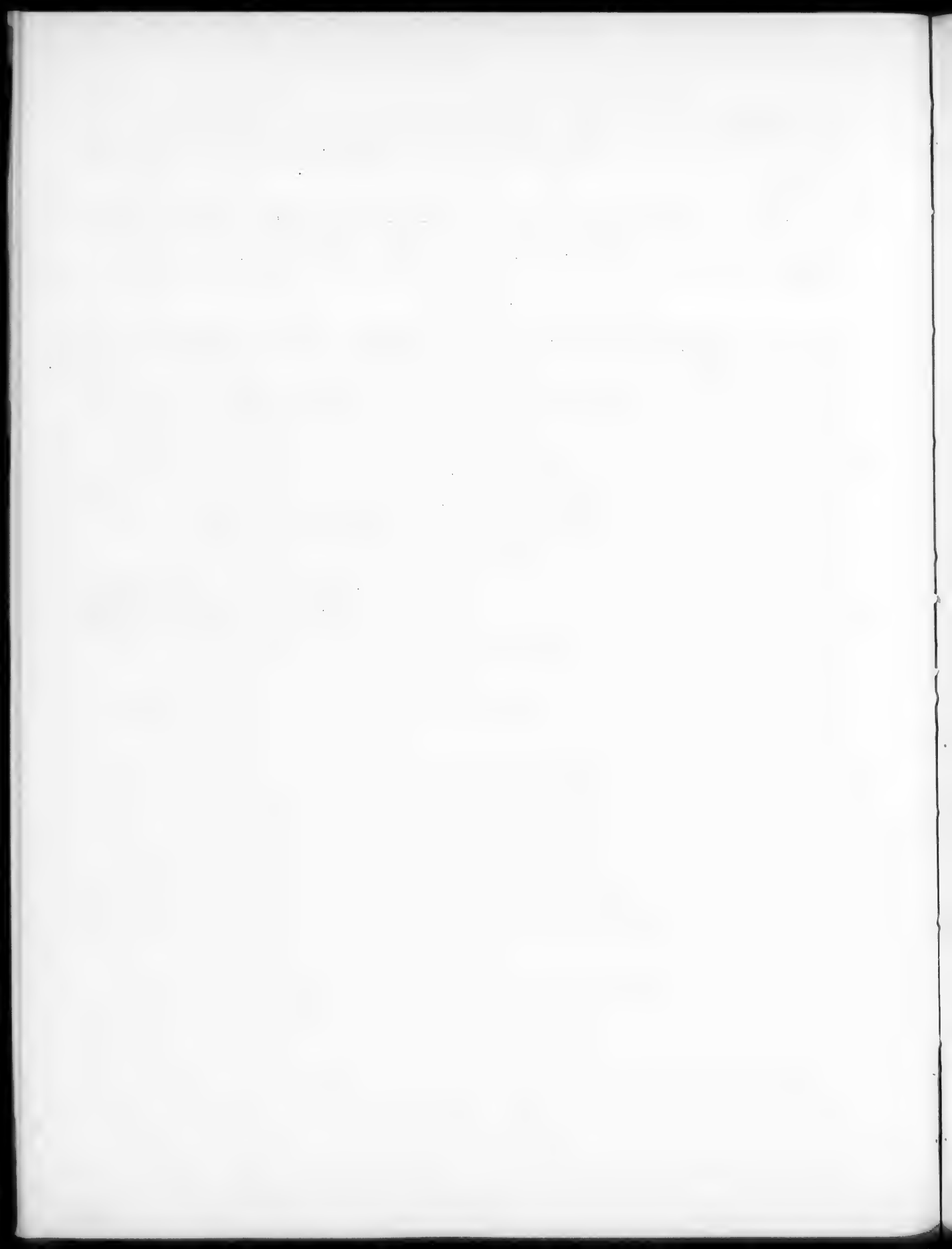
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INVESTIGATION OF THE ALKALOIDS FROM THE PLANT LEONTICE EWERSMANNII BGE.

II. THE DECOMPOSITION PRODUCTS OF TASPINE

T. F. Platonova and A. D. Kuzovkov

The alkaloid taspine was isolated from the shoot portions of the *Leontice* plant. On the basis of analytical data and functional group determinations, it was assigned the formula $C_{26}H_{19}O_6N$, or



We continued our investigation of this alkaloid with an attempt to determine the nature of its carbon skeleton. Distillation of taspine with zinc dust gave fluorene. Fusion of taspine with solid caustic potash gave a crystalline substance with the composition $C_{12}H_{10}O_4$ (m.p. 217.5-218.5°) with four phenolic hydroxyls, as shown by its elementary composition, hydroxyl group determination, the formation of a tetraacetyl derivative (m.p. 87-88.5°) and of products of methylation by means of diazomethane: $C_{12}H_6(OCH_3)_4$ (m.p. 100.5-101.5°) and



Oxidation of the substance $C_{12}H_{10}O_4$ gave 2,3-dihydroxybenzoic acid, and distillation with zinc dust gave diphenyl.

Therefore the substance $C_{12}H_{10}O_4$ is 2,3,x',y'-tetrahydroxydiphenyl. Our tetrahydroxydiphenyl isomer differs from those described in the literature. The formation of a tetrahydroxydiphenyl isomer and of fluorene leads to the supposition, which obviously requires further confirmation, that taspine may be regarded as a diphenyl derivative.

In our first communication on taspine the view was put forward that the amino group in the molecule of this alkaloid is in an open chain. This was confirmed as follows. Boiling of taspine with hydrobromic acid resulted in saponification of the lactone group, and of methoxyl and methylenedihydroxy groups, and an amino acid named taspinic acid was formed. The hydrobromide of this acid melts at 298° and has the composition $C_{17}H_{17}O_7N \cdot HBr$.

The oxidation of taspinic acid by potassium permanganate in sulfuric acid solution gave β -dimethylaminopropionic acid (m.p. 143-144°, hygroscopic), its hydrochloride (m.p. 186-188°), reineckate (m.p. 164-175°), ethyl ester (b.p. 62-64° at 15 mm), ethyl ester hydrochloride (m.p. 143-145°) and the methiodide of the ethyl ester (m.p. 175°). The formation of β -dimethylaminopropionic acid indicates the presence in taspinic acid, and possibly also in taspine, of the side chain $CH_2CH_2 \cdot N(CH_3)_2$, and may perhaps be attributed to the fact that oxidation results in the destruction of aromatic nuclei (containing a large number of phenolic groups) and the formation of the carboxyl group of β -dimethylaminopropionic acid at the carbon atom of the aromatic ring which is linked to the side chain.

EXPERIMENTAL

Distillation of taspine with zinc dust. 5 g of taspine was distilled by the well-known method with 50 g of zinc dust in a stream of dry hydrogen. Volatile amines were evolved, and were absorbed in 10% hydrochloric acid solution. After cooling, the solid and liquid reaction products were extracted with ether. Bases were removed from the ether solution by shaking it with 2% hydrochloric acid and washing with water. After removal of the ether, 50 ml of alkaline water was added to the residue and the volatile products were distilled in steam. The distillate was twice extracted with ether. The extract, after drying and removal of solvent, gave 0.07 g of a partly crystalline residue from which a colorless crystalline substance was sublimed at low pressure (20 mm) at 100°, the melting point of which after 2-fold recrystallization from alcohol was 108.5-109.5°. A sample mixed with fluorene did not give a melting point depression.

The hydrochloric acid solution of the amines was evaporated almost to dryness. When picric acid was added to the residue, a crystalline picrate was precipitated, m.p. 225-226° (from alcohol).

Found %: C 37.73; H 4.62; N 19.69. $C_9H_{12}O_7N_4$. Calculated %: C 37.51; H 4.19; N 19.44.

Fusion of taspine with solid caustic potash. 4 g of taspine and 16 g of caustic potash were heated together in a round-bottomed flask of 500 ml capacity, in a stream of dry nitrogen till the mixture fused into a homogeneous brown mass. The melt was dissolved in 150 ml of 10% sulfuric acid, the solution was filtered, and repeatedly extracted with ether. After removal of the ether 1.6 g of a crystalline substance was obtained. After 2-fold crystallizations from toluene fine needles were obtained, m.p. 217.5-218.5 g. Yield 0.7 g. The substance was soluble in ether, alcohol, and acetone, sparingly soluble in toluene.

3.511 mg sub.: 8.540 mg CO_2 ; 1.548 mg H_2O . 4.221 mg sub.: 10.243 mg CO_2 ; 1.913 mg H_2O . 5.188 mg sub.: 2.50 ml CH_4 (19.5°, 742 mm). 3.900 mg sub.: 1.85 ml CH_4 (19.5°, 742 mm). 0.0102 g sub.; 0.1022 g camphor; Δt 17.3°. Found %: C 66.38, 66.22; H 4.93, 5.07; OH 33.69, 33.16. M 231. $C_{12}H_{10}O_4$. Calculated %: C 66.05; H 4.62; 4OH 31.16. M 218.2.

Methylation of tetrahydroxydiphenyl. 0.75 g of tetrahydroxydiphenyl in 20 ml of ether was mixed with a solution of diazomethane in ether (from 8.5 g of nitrosomethylurea) and left 4 days. For separation of the phenolic and nonphenolic products the oily residue after removal of the ether was dissolved in 5% caustic soda solution and repeatedly extracted with ether.

The substances from the ether extract, after removal of the solvent, were dissolved in benzene and purified by shaking with 5% solution of alkali. After drying of the benzene extract and removal of the solvent, 0.18 g of a crystalline substance was obtained, which, after 2-fold recrystallization from 75% alcohol, melted at 100.5-101.5°.

3.909 mg sub.: 10.071 mg CO_2 ; 2.369 mg H_2O . 4.177 mg sub.: 10.766 mg CO_2 ; 2.489 mg H_2O . 3.613 mg sub.: 16.05 ml N $Na_2S_2O_3$. 3.158 mg sub.: 14.00 ml 0.02 N $Na_2S_2O_3$. Found %: C 70.31, 70.34; H 6.78, 6.77; OCH_3 45.31, 45.21. $C_{12}H_6(OCH_3)_4$. Calculated %: C 70.05; H 6.61; 4OCH₃ 45.24.

The aqueous alkaline solutions, after acidification and extraction with ether, yielded 0.25 g of a substance which, after 3-fold recrystallization from alcohol, melted at 127.5-128.5°.

3.552 mg sub.: 8.949 mg CO_2 ; 1.961 mg H_2O . 3.190 mg sub.: 8.040 mg CO_2 ; 1.770 mg H_2O . 7.583 mg sub.: 26.71 ml 0.02 N $Na_2S_2O_3$. 4.262 mg sub.: 14.92 ml 0.02 N $Na_2S_2O_3$. Found %: C 68.75, 68.78; H 6.18, 6.20; OCH_3 35.93, 35.71. $C_{12}H_6(OH)(OCH_3)_3$. Calculated %: C 69.24; H 6.19; 3OCH₃ 35.75.

Acetylation of tetrahydroxydiphenyl. 1.25 g of tetrahydroxydiphenyl and 20 ml of acetyl chloride were boiled under a reflux condenser for 1.5 hours. After removal of the excess acetyl chloride under vacuum, the reaction products (1.6 g) were dissolved in ether and repeatedly washed with 5% caustic soda solution to remove acid and phenolic impurities. Evaporation of the ether solution to a small volume resulted in the precipitation of 1.4 g of colorless needles, m.p. 87-88.5°. The melting point did not alter after crystallization.

4.480 mg sub.: 10.246 mg CO_2 ; 1.919 mg H_2O ; 3.423 mg sub.: 7.830 mg CO_2 ; 1.483 mg H_2O . Found %: C 62.41, 62.42; H 4.79, 4.84. $C_{12}H_6(OCOCH_3)_4$. Calculated %: C 62.18; H 4.69.

Oxidation of tetraacetyl tetrahydroxydiphenyl. 3.4 g of chromic anhydride was added to 1.2 g of tetraacetyl tetrahydroxydiphenyl in 10 ml of glacial acetic acid at 70° during 1.5 hours with constant stirring. The reaction mass was diluted with water to 150 ml and extracted 3 times with ether. The residue after removal of the ether was evaporated under vacuum to remove acetic acid, and dissolved in 5% aqueous ammonia. The solution was washed with ether and acidified with 10% sulfuric acid. Extraction with ether gave an acid (0.09 g) which, after sublimation under vacuum at 110-115° and crystallization from water, melted at 200-202°. Repetition of the sublimation and crystallization raised the m.p. to 205-206°. Yield 0.05 g. A sample mixed with 2,3-dihydroxybenzoic acid produced no depression of melting point.

Found %: C 54.81, 54.50; H 4.42, 4.34. $C_7H_6O_4$. Calculated %: C 54.55; H 3.92.

Distillation of tetrahydroxydiphenyl with zinc dust. 1.9 g of tetrahydroxydiphenyl was distilled with 19 g of zinc dust in a stream of dry hydrogen. The reaction products were dissolved in ether, shaken with 2% caustic soda solution to remove acids and phenols, and washed with water. After removal of the ether 0.27 g of resinous crystals remained, which, after sublimation at 100° and 2-fold recrystallization from alcohol, consisted of shiny plates, m.p. 65.5-67°. A sample mixed with diphenyl melted at the same temperature.

Found %: C 93.43; H 6.50. $C_{12}H_{10}$. Calculated %: C 93.46; H 6.53.

Preparation of taspinic acid. 20 g of taspine and 200 ml of hydrobromic acid ($d = 1.48$) were boiled together for 3 hours till the alkaloid dissolved completely. The reaction product, which crystallized in the form of needles

when the reaction mass was cooled, was filtered, washed with acetone, and recrystallized from dilute hydrobromic acid. Yield 23 g, m.p. 298° (decomp.).

3.373 mg sub.: 5.980 mg CO₂; 1.327 mg H₂O. 4.340 mg sub.: 7.729 mg CO₂; 1.778 mg H₂O. 9.601 mg sub.: 0.270 ml N₂ (23°, 735 mm). 5.861 mg sub.: 0.166 ml N₂ (23°, 735 mm). Found %: C 48.38, 48.60; H 4.40, 4.58; N 3.14, 3.16. C₁₇H₁₈O₇NBr. Calculated %: C 47.68; H 4.23; N 3.26.

Taspininic acid was isolated in the form of a bulky amorphous precipitate by the neutralization of 23 g of the hydrobromide in 170 ml of water with 5% caustic soda (to a weakly acid reaction to methyl red). The precipitate was washed with water and dried at 100° in vacuum. Yield 19 g. Taspininic acid is insoluble in water, alcohol, or acetone, and dissolves in acids and alkalis.

Oxidation of taspininic acid. 1.9 liters of 3.5% potassium permanganate solution was added to a filtered solution of 19.5 g of taspininic acid in 3.9 liters of 5% H₂SO₄ with vigorous stirring for 6 hours. The addition was stopped when a manganese dioxide precipitate which did not disappear in the course of an hour was formed. The precipitate was filtered off; the transparent slightly yellowish filtrate was evaporated under vacuum to a volume of about 2 liters, made alkaline with 40% caustic soda, and again acidified with hydrochloric acid (1:1) against methyl orange, and then evaporated to dryness. The reaction products were extracted 3 times from the residue, which contained large quantities of inorganic salts, by anhydrous alcohol acidified with gaseous HCl. After removal of the alcohol the residue was dissolved in 60 ml of water and shaken with ether to remove acid impurities. The aqueous solution was made alkaline with caustic soda (solution A), and organic bases were extracted with ether. The ether extract was dried with solid caustic potash, and alcoholic HCl was added to give the hydrochloride which, after crystallization from alcohol, was in the form of colorless needles, m.p. 143-145°. Yield 2.4 g.

3.800 mg sub.: 6.469 mg CO₂; 3.020 mg H₂O. 4.359 mg sub.: 7.402 mg CO₂; 3.482 mg H₂O. 6.255 mg sub.: 0.35 ml N₂ (17°, 740 mm). 6.55 mg sub.: 1.88 ml 0.02 N NH₄CNS. 8.122 mg sub.: 2.30 ml 0.02 N NH₄CNS. Found %: C 46.46, 46.34; H 8.89, 8.94; N 6.44; Cl 20.35, 20.08. C₇H₁₅O₂N·HCl. Calculated %: C 46.29; H 9.08; N 7.71; Cl 19.52.

The base was obtained from the hydrochloride (2.3 g) in the usual way, b.p. 62-64° (15 mm). Yield 0.82 g.

Methiodide. 0.3 g of methyl iodide was added to 0.3 g of the base, and a violent reaction took place with the formation of a crystalline substance. After recrystallization from alcohol this had m.p. 175°, fine needles, yield 0.46 g.

12.720 mg sub.: 26.40 ml 0.01 N Na₂S₂O₃. 7.848 mg sub.: 16.50 ml 0.01 N Na₂S₂O₃. Found %: I 43.92, 44.49. C₇H₁₅O₂N·CH₃I. Calculated %: I 44.19.

Saponification of the base. 0.1 g of the base was heated for 1 hour with 2 ml of 5% caustic soda solution at 100° in a sealed tube. The solution was cooled, acidified with 20% sulfuric acid, and washed by shaking with ether; the addition of a solution of Reinecke salt gave the crystalline reineckate which, after being washed with water and dried in a vacuum dessicator, melted at 168-174°.

The addition of an aqueous solution of 5 g of Reinecke salt saturated at 60° to solution A after acidification with hydrochloric acid (1:1) gave the crystalline reineckate which, after being washed with water and dried in a vacuum dessicator, melted at 164-175°. Yield 5.4 g. A mixture with the reineckate obtained previously after saponification of the base melted at the same temperature.

Preparation of β-dimethylaminopropionic acid. 4.6 g of the reineckate was triturated with 100 ml of 10% hydrochloric acid, and the Reinecke acid was extracted by ethyl acetate. The ethyl acetate extract was washed 3 times with 5% hydrochloric acid. The acid extracts were added to the main aqueous hydrochloric acid extract, decolorized by charcoal, and evaporated to dryness under vacuum. The partly crystallized residue was dissolved in 20 ml of anhydrous alcohol and filtered. Ether was added to isolate the crystalline hydrochloride. After three crystallizations from a mixture of alcohol and ether the yield was 0.65 g, fine needles, m.p. 181-182°. The product is easily soluble in water, less so in alcohol, and is insoluble in acetone or ether.

4.660 mg sub.: 6.690 mg CO₂; 3.118 mg H₂O. 4.672 mg sub.: 6.700 mg CO₂; 3.210 mg H₂O. 8.197 mg sub.: 0.608 ml N₂ (22°, 731 mm). 11.240 mg sub.: 3.54 ml 0.02 N NH₄CNS. Found %: C 39.18, 39.13; H 7.49, 7.69; N 8.25; Cl 22.33. C₅H₁₁O₂N·HCl. Calculated %: C 39.07; H 7.87; N 9.11; Cl 23.08.

0.5 g of the hydrochloride in 5 ml of water was shaken with moist silver oxide (from 0.66 g AgNO₃), the solution was filtered, silver ions were removed by hydrogen sulfide, and the solution was evaporated to dryness under a

vacuum; the crystalline extract was twice crystallized from acetone. The yield was 0.2 g of a colorless, highly hygroscopic substance, needles, m.p. 143-144°. A sample mixed with β -dimethylaminopropionic acid melted at the same temperature.

3.468 mg sub.: 6.445 mg CO₂; 2.852 mg H₂O. 5.430 mg sub.: 10.108 mg CO₂; 4.588 mg H₂O. 8.720 mg sub.: 0.890 ml N₂ (19°, 748 mm). 7.849 mg sub.: 6.60 ml 0.01 N H₂SO₄ (Kjeldahl). Found %: C 50.72, 50.80; H 9.20, 9.45; N 11.74, 11.77. C₅H₁₁O₃N. Calculated %: C 51.26; H 9.46; N 11.95.

The hydrochloride of the amino acid was prepared by the addition of alcoholic HCl to a solution of the acid in anhydrous alcohol. Recrystallization from alcohol gave colorless prisms, m.p. 186.5-188°. A sample mixed with β -dimethylaminopropionic acid hydrochloride melted at 186.5-188°.

SUMMARY

The decomposition products of taspine were investigated, and the supposition is put forward that the alkaloid is a diphenyl derivative and contains a CH₂CH₂N(CH₃)₂ side chain.

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* T. p. = C. B. Translation pagination.

SYNTHESIS OF ALIPHATIC ELEMENTOORGANIC COMPOUNDS BY THE DIAZO METHOD

VII. SYNTHESIS OF COMPOUNDS OF GROUP V ELEMENTS - ORGANOPHOSPHORUS COMPOUNDS.

TRICHLOROMETHYLCHLOROPHOSPHINIC ACID AND ITS TRANSFORMATIONS

A. Ya. Yakubovich and V. A. Ginsburg

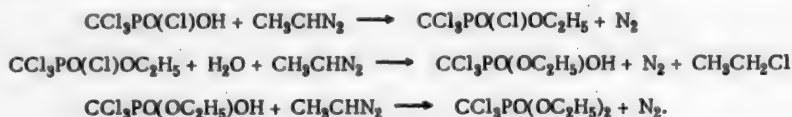
Since phosphorus trichloromethyltetrachloride has become an easily available substance due to the diazo method for the synthesis of chloromethyldichlorophosphine [1], it appeared desirable to attempt the preparation of trichloromethylphosphinic acid not from its esters, as was described earlier by the present authors [2], but by direct hydrolysis of CCl_3PCl_4 . As was already noted [2] the hydrolysis of this tetrachloride in cold water is slow and incomplete, and therefore subsequently the hydrolysis was effected with water heated to 60-70°. In these conditions CCl_3PCl_4 is hydrolyzed rapidly with considerable evolution of heat. When the solution was evaporated in a vacuum at temperatures not above 40-50° and the substance then dried thoroughly in a desiccator over P_2O_5 , a crystalline product was obtained, but its properties differed sharply from those of trichloromethylphosphinic acid formed by saponification of its esters. The substance described, which was 10 times as soluble in carbon tetrachloride and benzene and which deliquesced in the presence of moisture, had m.p. 79°, and considerable depression of melting point was observed when a sample was mixed with known trichloromethylphosphinic acid (m.p. 87°). Titration of aqueous solutions of this substance showed that it is not a di-, but a monobasic acid. This same acid is formed by the hydrolysis of the dichloroanhydride of trichloromethylphosphinic acid in analogous conditions.

Analytical data showed that this acid (with m.p. 79°) contained four chlorine atoms in the molecule, and corresponded to the empirical formula $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$. However, the unusual nature of such a molecule, with a hydroxyl group together with an acid chloride atom at the phosphorus atom, and also the unusual stability of the "acid halide" chlorine to hydrolysis, led us to undertake further researches in order to confirm the proposed structure of this compound. The following was established: water and 0.5 N aqueous solution of caustic potash in the cold do not split off halogen from this acid; when a sample of the substance is boiled a long time (4 hours) with 0.5 N aqueous caustic potash solution, all 4 halogen atoms are split off. In analogous conditions trichloromethylphosphinic acid also decomposes completely. When an aqueous solution of the acid with m.p. 79° is heated with silver nitrate solution, a precipitate is formed. When concentrated aqueous solutions of these reagents are used in the cold, the precipitate forms slowly (after several days), and the precipitate consists of AgCl and the disilver salt of trichloromethylphosphinic acid, $\text{CCl}_3\text{PO}(\text{OAg})_2$, which are formed in equimolecular proportions. If the acid with m.p. 79° is heated in an ampoule with hydrochloric acid in conditions for the saponification of trichloromethylphosphinic acid esters, trichloromethylphosphinic acid with m.p. 87° is formed. When a mixture of the acid with m.p. 79° and excess aniline in benzene is allowed to stand a long time at room temperature, no anilide formation or hydrogen chloride evolution occurs.

When this reaction is carried out in solution, dilution with a large amount of benzene results in the quantitative precipitation of an aniline salt of the acid with m.p. 79°, which differs from the aniline salts of trichloromethylphosphinic acid both by its melting point and by its titration behavior with methyl orange and phenolphthalein (monobasic), and by its much higher solubility in organic solvents (alcohol, aniline, acetone). The analytical data for this salt agreed with the calculated values for the compound $\text{CCl}_3\text{PO}(\text{Cl})\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$.

When the acid with m.p. 79° is treated with excess (3 moles: 1 mole) of a moist solution of diazoethane or diazomethane in ether, acid esters of the type $\text{CCl}_3\text{PO}(\text{OR})\text{OH}$ are formed, which have the properties of monobasic acids and which yield aniline salts of the type $\text{CCl}_3\text{PO}(\text{OR})\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$, which are identical with the salts obtained by the treatment of the dimethyl and diethyl esters of trichloromethylphosphinic acid with aniline [2]. Vacuum distillation of the acid ethyl ester formed is accompanied by decomposition, and the distillation products are found to contain the fully substituted ethyl ester of trichloromethylphosphinic acid, formed in low yield. A second treatment of the acid ethyl ester with diazoethane leads to the formation of the complete ester in a yield of 50-70% on the original acid ester.

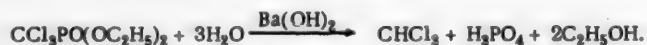
Since, as we have repeatedly observed, moist solutions of aliphatic diazo compounds are active hydrolytic agents, the course of the above reactions is explained as follows:



Here the removal of hydrogen chloride from the reaction zone apparently favors the relatively rapid hydrolysis of the intermediately formed chloro ester.

For a final determination of the structure of the acid ester of trichloromethylphosphinic acid it was desirable to obtain it from a definitely known compound — the diethyl ester of trichloromethylphosphinic acid — and to compare the two products. With this aim in view, the fully substituted ethyl ester of trichloromethylphosphinic acid was saponified in mild conditions — by aqueous caustic baryta solution at 50-60° — and also slowly saponified with the aid of hydrochloric acid at room temperature.

The first method did not give the desired results, as it was found that at 50-60° the original ester is quantitatively decomposed by baryta solution to form chloroform and phosphoric acid

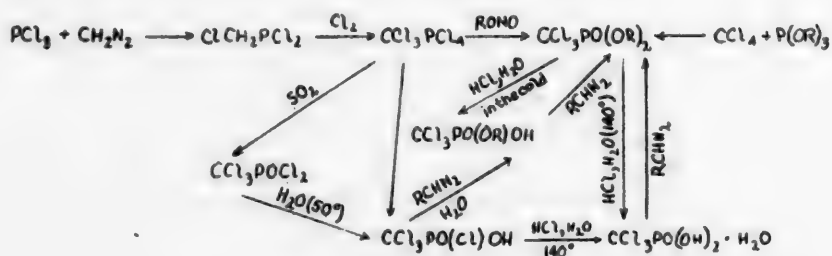


The second method, when the diethyl ester was saponified by hydrochloric acid at room temperature over a period of three months, gave the expected acid ester $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)\text{OH}$ which, with aniline, formed a salt identical with the aniline salt obtained by the diazoethane treatment of the acid with m.p. 79°, as described above.

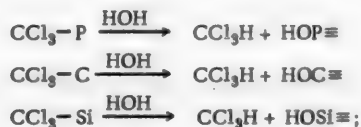
In order to establish whether the acid with m.p. 79° has a structure similar to that of trichloromethylphosphinic acid, and only differs from it in having a difficultly hydrolyzed chlorine atom instead of a hydroxyl group at the phosphorus atom, it was of interest to attempt to convert the acid with m.p. 87°, or its derivatives, into the acid with m.p. 79°. Treatment of $\text{CCl}_3\text{PO}(\text{OH})_2$ with phosphorus pentachloride or thionyl chloride did not answer the problem. This gave organophosphorus compounds of a polymeric type, which upon treatment with water were converted into an unknown organophosphorus acid with m.p. 109-110°, which was not studied further. However, the reaction of the diethyl ester of trichloromethylphosphinic acid with phosphorus pentachloride yielded an acid chloride which after hydrolysis formed an acid with m.p. 79°, identical with the acid formed by the hydrolysis of phosphorus trichloromethyltetrachloride. It must be pointed out that this reaction between the ester of trichloromethylphosphinic acid and PCl_5 does not take place in the cold, but occurs only at 150°.

A final confirmation of the structure of the acid with m.p. 79° was provided by the results of optical analysis of trichloromethylphosphinic compounds. Infrared spectrum study of the acid with m.p. 79° showed the presence of the following bonds in the molecule: a) $\text{P}=\text{O}$ (1261 cm^{-1}); b) $\text{C}-\text{Cl}$ (1529 cm^{-1}); c) $\text{O}-\text{H}$ (3400 cm^{-1}); d) $\text{P}-\text{Cl}$ (combinational scattering spectrum, 487 cm^{-1}). These results fully confirm the validity of the proposed structure for the acid with m.p. 79°, as $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$.

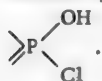
By the above study of the chemical properties of the trichloromethylphosphine derivatives obtained from chloromethyldichlorophosphine and from the esters of trichloromethylphosphinic acid it was possible to establish the relationship between them which may be expressed by the following scheme:



Study of the chemistry of trichloromethyl phosphorus compounds led to the general conclusion that the introduction of three chlorine atoms at the carbon atom of methylphosphine derivatives results in a number of peculiarities in their chemical behavior, of which the most important are the following: a) a sharp decrease in the activity of the P-Cl bond to hydrolysis and ammonolysis (with aniline); b) weakening of the C-P bond to the action of alkalis, when the $\text{CCl}_3\text{-P}$ group behaves like $\text{CCl}_3\text{-C}$ and $\text{CCl}_3\text{-Si}$, which in many instances are easily split by the action of alkalis:



c) there is also a resemblance between trichloromethylphosphine compounds and substances of the chloral type in the tendency of trichloromethylphosphinic acid to form stable hydrates [2]; d) the introduction of a halogen atom into the methyl group of methylphosphinic acid leads to an increase in the acidity of these substances, so that chloro-bromomethylphosphinic and trichloromethylphosphinic acids acquire the power of forming dianiline salts; e) the presence of a CCl_3 group attached to the phosphorus leads to the possibility of an unusual molecule of a semi acid-chloride type, which has both a halogen atom and a hydroxyl group simultaneously linked to the phosphorus atom,



We must note a certain resemblance between the behavior of the acid chlorides of trichloromethylphosphinic acid and compounds of the "Boyd's chloroanhydride" type which are acid dichlorides of triarylmethylphosphinic acids. These latter are so resistant to hydrolysis that the acid chloride atoms are not hydrolyzed even after many hours of boiling with alkali. The second chlorine atom, linked to phosphorus is particularly inert in "Boyd's chloroanhydride"; this, as was shown by A. E. Arbuzov and B. A. Arbuzov [3] does not react even with such substances as alkali metal alcoholates. It is seen that the presence of three negative chlorine atoms linked to carbon in a methyl group confers properties on the molecule of the acid chloride of methylphosphinic acid which are similar to the properties produced by the introduction of three aryl radicals into the methyl group.

EXPERIMENTAL

Hydrolysis of phosphorus trichloromethyltetrachloride. Preparation of trichloromethylchlorophosphinic acid— $\text{CCl}_3\text{P}(\text{Cl})\text{OH}$. Phosphorus trichloromethyltetrachloride, prepared by the chlorination of 20 g of chloromethylidichlorophosphine, was gradually added to 30 ml of water with stirring. The reaction was sluggish at first, but as the water became warm the subsequent hydrolysis terminated very rapidly and the tetrachloride dissolved completely. The water was removed from the aqueous solution under vacuum at a temperature not higher than 30–40°, the crystals formed were pressed out on a porous plate, and the remaining moisture was removed in a vacuum desiccator over P_2O_5 .

The yield was 27 g of colorless needle shaped crystals which melted at 79° after recrystallization from benzene (solubility 10 g in 200 ml of benzene at 70°). The substance is easily soluble in hot CCl_4 (17 g in 200 ml), badly in cold, and deliquesces in water, alcohol, and acetone.

3.915 mg sub.: 0.789 mg CO_2 ; 0.602 mg H_2O . 3.890 mg sub.: 0.758 mg CO_2 ; 0.534 mg H_2O . 0.0344 g sub. (sealed tube): 5.87 ml 0.1 N AgNO_3 . 0.030 g sub. (sealed tube): 5.51 ml 0.1 N AgNO_3 . 0.0486 g sub.: 0.4004 g molybdate. 0.1052 g sub.: 0.8799 g molybdate. 0.1698 g sub.: 7.30 ml 0.1 N KOH (methyl orange); 7.83 ml (phenylphthalein). 0.1562 g sub.: 6.65 ml 0.1 N KOH (methyl orange); 7.05 ml (phenylphthalein). Found %: C 5.49, 5.39; H 1.72, 1.53; Cl total 64.85, 65.11; P 13.62, 13.78. Equiv. (methyl orange) 230, 232, (phenylphthalein) 214, 218. $\text{CCl}_3\text{P}(\text{Cl})\text{OH}$. Calculated %: C 5.50; H 0.46; Cl total 65.14; P 14.22. Equiv. 218.

Determination of the molecular weight in acetophenone gave a high value (270). The substance forms no insoluble Ag salts in the cold; prolonged heating of the acid $\text{CCl}_3\text{P}(\text{Cl})\text{OH}$ and AgNO_3 leads to the formation of a precipitate consisting of $\text{CCl}_3\text{P}(\text{OAg})_2$ and AgCl , formed in equimolecular proportions.

Hydrolysis of the acid dichloride of trichloromethylphosphinic acid. 20 g of $\text{CCl}_3\text{POCl}_2$ was hydrolyzed by 30 ml of water warmed to 50°, and excess water was then removed under vacuum. Careful drying yielded 17 g of needle-like crystals, m.p. 79°; the substance was identical with the acid obtained by the hydrolysis of phosphorus trichloromethyltetrachloride.

Preparation of the aniline salt of trichloromethylchlorophosphinic acid $\text{CCl}_3\text{PO}(\text{Cl})\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$. 3 g of aniline was added to a solution of 2 g of $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$ in 260 ml of benzene and the mixture left for twenty-four hours. The precipitate was then filtered off and washed with benzene. Fine needles, m.p. 190-191° (decomp.).

4.500 mg sub.: 4.530 mg CO_2 ; 1.380 mg H_2O . 5.150 mg sub.: 5.163 mg CO_2 ; 1.565 mg H_2O . 5.805 mg sub.: 0.2450 ml N_2 (26°, 743 mm). 5.500 mg sub.: 0.2254 ml N_2 (26°, 743 mm). 9.450 mg sub.: 2.420 ml 0.05 N AgNO_3 . 0.1202 g sub.: 3.90 ml 0.1 N KOH (phenolphthalein). 0.1250 g sub.: 4.00 ml 0.1 N KOH. Found %: C 27.45, 27.43; H 3.43, 3.41; N 4.77, 4.65; Cl 45.45. Equiv. 307. $\text{CCl}_3\text{PO}(\text{Cl})\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$. Calculated %: C 27.10; H 2.65; N 4.51; Cl 45.80. Equiv. 312.

Hydrolysis of trichloromethylchlorophosphinic acid. Conversion of the acid with m.p. 79° into trichloromethylphosphinic acid. 1 g of the acid $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$ with m.p. 79° was heated for 3 hours at 140° with 5 ml of 15% hydrochloric acid. After removal of water under vacuum the crystalline mass was dried over P_2O_5 and recrystallized from benzene. Needles, m.p. 87°. The substance forms an insoluble silver salt which explodes on heating. A sample mixed with known trichloromethylphosphinic acid gave no melting point depression.

Reaction of trichloromethylchlorophosphinic acid with diazoethane. a) Preparation of the acid ethyl ester of trichloromethylphosphinic acid $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)\text{OH}$. A solution of 5.5-6 g (3 moles) of diazoethane in 300 ml of ether (the ether solution of diazoethane was not dried in this instance) was added dropwise to 6 g (1 mole) of the acid $\text{CCl}_3\text{PO}(\text{Cl})\text{OH}$ with m.p. 79° in 50 ml of ether at -10°. The decomposition of the diazo compound was vigorous at first and then slowed down. After the diazo compound disappeared from the solution the ether solution was dried over sodium sulfate and the ether distilled off with the aid of a fractionating column. The residue was 7.2 g of a thick faintly colored liquid which slowly dissolved in water to give an aqueous solution with an acid reaction. The product was the impure acid ethyl ester of trichloromethylphosphinic acid.

0.0538 g sub.: 15.45 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. 0.0715 g sub.: 20.06 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. Found %: OC_2H_5 21.56, 21.06. $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)\text{OH}$. Calculated %: OC_2H_5 19.85.

When distilled in vacuum the acid ester decomposed with the formation of a small amount of the diethyl ester of trichloromethylphosphinic acid with b.p. 122-123° at 12 mm, d_4^{14} 1.3670, n_D^{20} 1.4610 and of other lower-boiling products.

b) Preparation of the aniline salt of the acid ethyl ester of trichloromethylphosphinic acid. 2 g of aniline was added to a mixture of 1 g of the acid ester (see the previous experiment) and 25 ml of benzene. Fine small needles of the salt were immediately precipitated. After 4 hours the precipitate was separated off and washed with benzene. M.p. 175-176° (decomp.); a sample mixed with the substance obtained by another method previously [2] gave no melting point depression.

0.0512 g sub.: 9.34 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. 0.0183 g sub.: 3.57 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. 0.1027 g sub.: 3.24 ml 0.1 N KOH. 0.1488 g sub.: 4.73 ml 0.1 N KOH (phenolphthalein). Found %: OC_2H_5 13.54, 14.66. Equiv. 317, 315. $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$. Calculated %: OC_2H_5 14.04. Equiv. 320.5.

c) Reaction of the acid ethyl ester of trichloromethylphosphinic acid with diazoethane. A solution of 2.7 g (3 moles) of diazoethane in 120 ml of ether was added to a solution of 4 g (1 mole) of the acid ethyl ester of trichloromethylphosphinic acid (prepared as described in Experiment "a") in 50 ml of ether at -5°. After the excess diazoethane decomposed overnight and the solution became colorless, it was dried with sodium sulfate and the ether was distilled off. The residue (4.5 g) was fractionated. Most of the liquid distilled at 115-130° (13 mm). A second fractionation yielded the diethyl ester of trichloromethylphosphinic acid with b.p. 122° (12 mm), d_4^{14} 1.3690, n_D^{20} 1.4620.

0.0702 g sub.: 32.81 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. 0.0862 g sub.: 40.88 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. Found %: OC_2H_5 34.87, 35.32. $\text{CCl}_3\text{PO}(\text{OC}_2\text{H}_5)_2$. Calculated %: OC_2H_5 35.22.

Preparation of trichloromethylchlorophosphinic acid from the diethyl ester of trichloromethylphosphinic acid by the action of phosphorus pentachloride. a) Preparation of trichloromethylchlorophosphinic acid. 15 g of PCl_5 was added to 4 g of the diethyl ester of trichloromethylphosphinic acid and the mixture heated for 1 hour at 150°. 5 g of POCl_3 was driven off in the process. The residue solidified on cooling; treatment with sulfur dioxide converted it into a liquid. After removal (under vacuum) of the last remains of phosphorus oxychloride a viscous mass remained, which was extracted with 10 ml of hot water and the water removed under vacuum, when 2.5 g of needle-shaped crystals remained in the flask. M.p. 78-79° after recrystallization from benzene. No melting point depression was found when a sample of the crystals was mixed with known trichloromethylphosphinic acid.

b) Reaction of trichloromethylphosphinic acid with PCl_5 and SOCl_2 . The reactions between trichloromethylphosphinic acid and PCl_5 or SOCl_2 do not lead to the formation of the acid dichloride of trichloromethylphosphinic acid. After removal of POCl_3 or excess SOCl_2 under vacuum the residue was a solid mass of organophosphorus compounds insoluble in organic solvents. Treatment of this mass with water yields, after removal of the water under vacuum, a monobasic acid, m.p. 109-110°, with an equivalent weight of 190-200; this compound was not studied further.

Saponification of the diethyl ester of trichloromethylphosphinic acid by caustic baryta. 4.5 g of $\text{CCl}_3\text{P}(\text{OC}_2\text{H}_5)_2$ was added dropwise at 60-80° to a suspension of 3 g of caustic baryta in 25 ml of water. There was an immediate reaction, chloroform being given off and collected in a receiver. The total yield was 2.2 g of chloroform, b.p. 61-62°, which gave the characteristic "isonitrile" reaction. Phosphate ions (by the reaction with ammonium molybdate) were detected qualitatively in the aqueous solution.

Saponification of the diethyl ester of trichloromethylphosphinic acid by hydrochloric acid in mild conditions. 4 g of $\text{CCl}_3\text{P}(\text{OC}_2\text{H}_5)_2$ and 15% of hydrochloric acid were sealed in an ampoule and left at room temperature for 3 months. At the end of that time the reaction mixture was still separated into two layers. The ampoule was opened, the lower layer was combined with the residue obtained when water was removed under vacuum from the upper layer, the whole was dissolved in alcohol, and 2 g of aniline was added to the solution. 2.5 g of a precipitate was formed which, upon recrystallization from water formed needle-shaped crystals with m.p. 176° (decomp.). A sample mixed with the product obtained in the previous experiment showed no depression of melting point.

3.813 mg sub.: 4.675 mg CO_2 ; 1.462 mg H_2O . 13.605 mg sub.: 2.600 ml 0.05 N AgNO_3 . 6.025 mg sub.: 0.2580 ml N_2 (23°, 746 mm). Found %: C 33.34; H 4.30; Cl 34.06; N 4.85. $\text{CCl}_3\text{P}(\text{OC}_2\text{H}_5)_2\text{OH} \cdot \text{C}_6\text{H}_5\text{NH}_2$. Calculated %: C 33.67; H 4.05; Cl 33.23; N 4.37.

SUMMARY

1. Trichloromethylchlorophosphinic acid was prepared by the hydrolysis of phosphorus trichloromethyltetra-chloride and phosphorus trichloromethyl oxychloride. Its properties and some peculiarities of its transformations have been studied. The relationships and conversions in the series of phosphorus trichloromethyl derivatives have been determined.

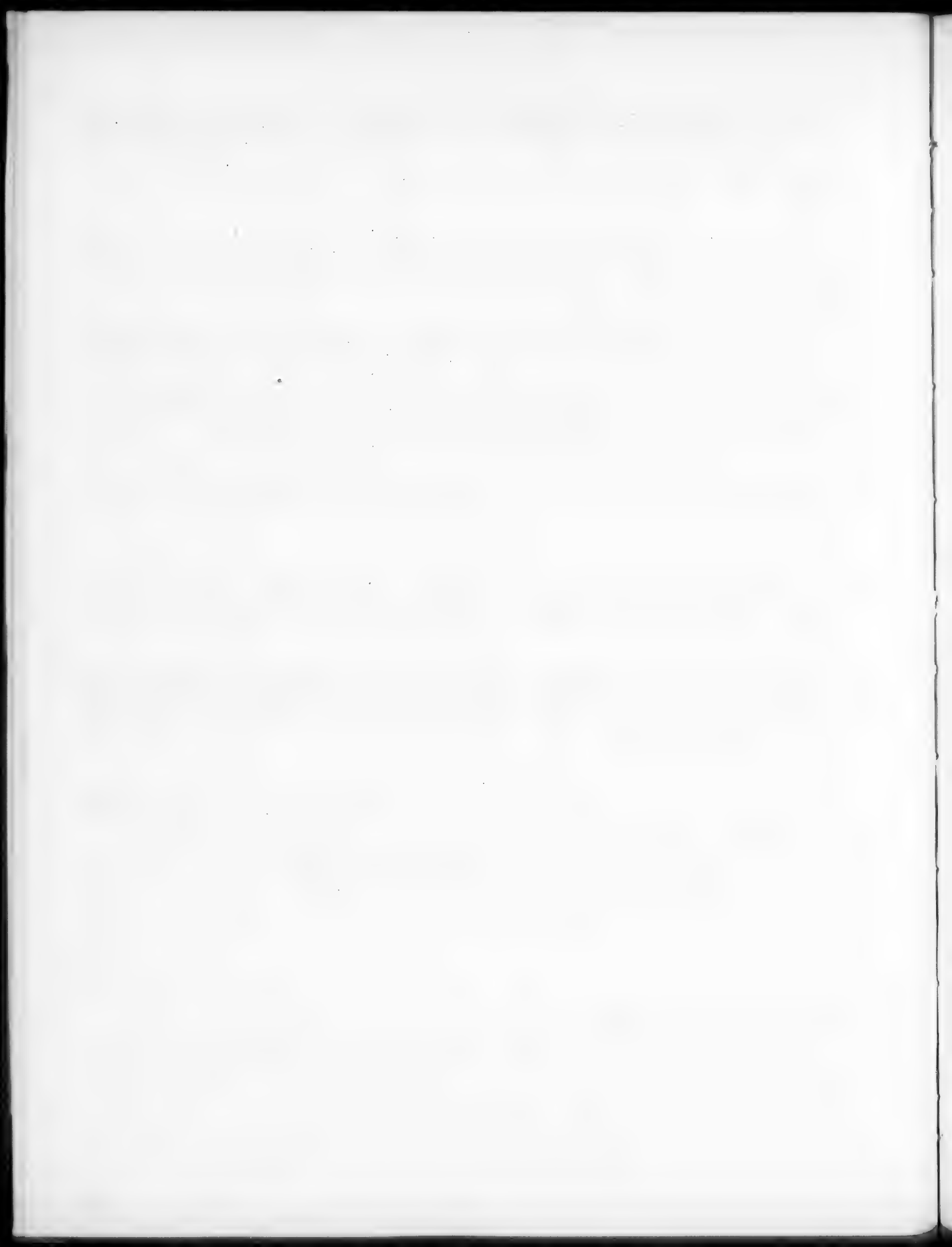
2. It is shown that the introduction of three chlorine atoms at the carbon atom of methylphosphine derivatives confers on the latter a number of peculiarities of chemical behavior. For example, the sensitivity of the P-Cl bond to hydrolysis and ammonolysis is reduced, the C-P bond is weakened toward the action of alkalis capable of splitting it with the formation of chloroform, and the phosphorus atom acquires the power of simultaneously retaining a halogen atom and a hydroxyl group.

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ADDITION OF NITROSYL CHLORIDE TO FLUORINATED OLEFINS. II

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In an earlier paper [1] the results of a study of the addition of nitrosyl chloride to chlorinated olefins were described; it was then established that in most instances the addition of nitrosyl chloride takes place in accordance with the polarity of the reacting bonds, so that the positive NO group is directed toward the negatively charged carbon atom joined to a double bond, while the negative halogen is directed toward the positively charged carbon atom.

It was of interest to determine the extent to which this orientation holds in the reactions between nitrosyl chloride and fluorinated ethylene derivatives.

The reaction of nitrosyl chloride with vinyl fluoride, 1,2-fluorochloroethylene, 1-fluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, and trifluorochloroethylene was studied.

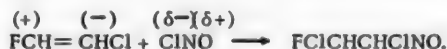
The addition of nitrosyl chloride to vinyl fluoride (and the other reactions) was brought about by the usual method — in ampoules at room temperature. The molar ratio of the reagents was 1:1. Fractionation of the reaction mixture yielded, in addition to a substance without nitrogen (1,2-dichloro-1-fluoroethane), a compound with b.p. 55.5° at 8 mm as the main reaction product. Analysis, molecular weight, and properties of this substance showed that it is a nitro-compound with the composition $C_2H_3ClFNO_2$ (yield 54%).

By analogy with the reaction with vinyl chloride, which proceeds normally, in the case of vinyl chloride the reaction should follow the scheme:



In fact, the nitrofluorochloroethane formed, as was shown by its positive nitrol reaction, proved to be 1-nitro-2,2-fluorochloroethane.

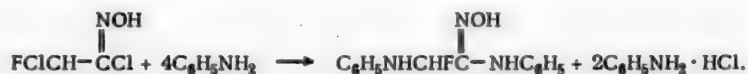
Nitrosyl chloride also reacted just as readily with 1,2-fluorochloroethylene; here the expected reaction should follow the scheme: •



This, in fact, occurs. The main product of the reaction between fluorochloroethylene and nitrosyl chloride is the acid chloride of fluorochloroacetohydroxamic acid, obtained in approximately 45% yield:



One proof, among others, of the structure of the compound as the acid chloride of a hydroxamic acid is its reaction with aniline, which occurs very readily with the formation of phenylaminofluoroacetohydroxamic acid anilide:



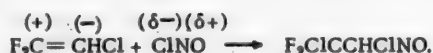
It is interesting to note that in reactions between nitrosyl chloride and halogenated ethylene derivatives which give rise to primary nitroso compounds (condensation with vinyl chloride, allyl chloride, etc.) the latter are oxidized

• Here and subsequently the signs (+) and (−) indicate only the relative electron density distributed in the C—C bond, that is, the direction of the dipole in this bond.

to nitro compounds. If, however, halogen is present at the carbon which becomes linked to the nitroso group (condensation with 1,2-fluorochloroethylene), a nitroso-oxime regrouping takes place with the formation of a hydroxamic acid halide. This is apparently to be explained by the specific influence of the α -chlorine atom, which has a greater inhibiting effect on oxidation than on the regrouping.

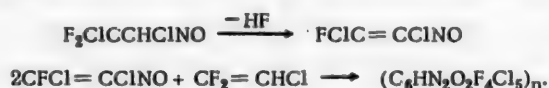
It is more difficult to determine the polarity of the C-C bond in the case of trihalogen substituted ethylene derivatives, when the halogen atoms are different, as for example, in 1,1-difluoro-2-chloroethylene or 1,1-dichloro-2-fluoroethylene.

Nevertheless, it may be assumed for difluorochloroethylene that the carbon atom charges are distributed as shown below. Consequently, the condensation of 1,1-difluoro-2-chloroethylene with nitrosyl chloride should be expected to follow the scheme:

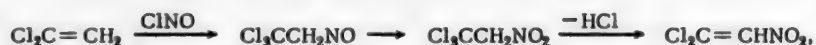


A study of this reaction showed that it takes a more complex course, and the main reaction product is a high molecular polymeric compound. When this polymer was heated in a vacuum it depolymerized and formed a substance with the composition $\text{C}_6\text{HO}_2\text{N}_2\text{Cl}_5\text{F}_4$, the structure of which was not studied further. In addition to the polymer, 1,1-dichloro-2,2,2-difluoronitroethane was formed in very low yield.

Apparently the polymer is formed as the result of changes in the normal addition product of nitrosyl chloride and difluorochloroethylene. These changes may be represented by the following series of equations:



This assumption is based both on the result of the previously studied analogous addition reaction between nitrosyl chloride and vinylidene chloride, leading to the formation of 1,1-dichloro-2-nitroethylene



and on data for the composition of the depolymerization product formed when the polymer is heated in a vacuum.

The normal course for the addition of nitrosyl chloride, put forward above, is also confirmed by the fact that the 1,1-dichloro-2,2,2-difluoroethane formed in the reaction is a stable compound and is obtained in very low yield, which indicates that the addition reaction between nitrosyl chloride and difluorochloroethane in a direction opposite to that dictated by the polarity of the reacting bonds is not the principal direction for the reaction between these substances.

The reaction between nitrosyl chloride and 1,1-dichloro-2-fluoroethylene in conditions analogous to those for the reaction with difluorochloroethylene takes place with the formation of 1,1-fluorochloro-2,2,2-dichloronitroethane in 55% yield and of a certain amount of a tertiary nitroso compound, apparently 1,1-fluorochloro-2,2,2-dichloronitrosoethane. This last compound could not be isolated in the pure state because the reaction mixture contained a nitrogen-free substance with a boiling point close to the boiling point of the nitroso compound formed. Thus, the main direction of the reaction between nitrosyl chloride and dichlorofluoroethylene follows the scheme:



It may be assumed that the reaction under consideration with 1,1-dichlorofluoroethylene proceeds normally in a direction which corresponds to the polarity of the reacting bonds, that is, $\text{FCH}=\text{CCl}_2$, as should follow if only from the fact that 1,1-fluorochloro-2,2,2-dichloronitroethane is the only condensation product formed in the process in a good yield.

Of the per-halogenated ethylene derivatives, the condensation of trifluorochloroethylene was studied, the carbon atoms of which are polarized as follows: $\text{F}_2\text{C}=\text{CFCl}$.

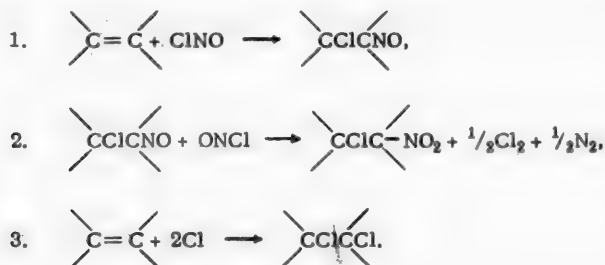
The addition of nitrosyl chloride to trifluorochloroethylene proceeds rather more slowly than in the other instances considered above; in addition to a nitroso compound and the chlorination product of trifluorochloroethylene,

the main reaction product here is trifluorodichloronitroethane. From the polarity of the ethylene bond in trifluorochloroethylene it may be assumed that the direction of the addition reaction and the structure of the nitro compound formed are given by the scheme:

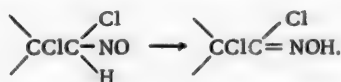


Thus, from the results of our study of addition reactions between nitrosyl chloride and halogenated ethylene derivatives it may be concluded that in most instances nitrosyl chloride is added on to the ethylene bond in the manner dictated by the polarities of the reacting bonds.

The general scheme of the addition reactions may be expressed as follows:



If an α -halogenated nitroso compound is formed as the result of nitrosyl chloride addition, the oxidation reaction is inhibited, and in the presence of a hydrogen atom a nitroso-oxime regrouping takes place:



With α -dihalogen nitroso compounds oxidation is also inhibited, and in addition to the nitro product the formation of intermediate nitroso compounds may be detected.

EXPERIMENTAL

The Experimental Section, in addition to a description of the addition reaction of nitrosyl chloride, contains details of the preparation of the original fluorochloroderivatives of ethane and ethylene. Most of these compounds have been described previously by others, who prepared them by various methods. Here we give only descriptions of syntheses in which the methods described in the literature were modified in some way. The constants of the fluorides obtained in most instances coincided with those cited in the literature. An exception was 1,1-difluoro-2-dichloroethylene, the boiling point of which, according to Henne and Ladd [2] is -2.4° , while in reality this substance boils at -15.5° .

1. Reaction of vinyl fluoride with nitrosyl chloride. a) **Preparation of vinyl fluoride.** A solution of sodium butylate (or amylate) prepared from 550 g of butyl alcohol and 17 g of sodium was placed in a round bottomed flask fitted with a dropping funnel and a reflux condenser. The condenser was connected to a trap immersed in freezing mixture (acetone + carbon dioxide). The sodium butylate solution was heated to a temperature close to 100° , and 74 g of chlorofluoroethane was added from the dropping funnel dropwise during 3-4 hours. The reaction products condensed in the cooled trap. During the reaction the temperature was so maintained that the liquid boiled gently; at the end of the addition of chlorofluoroethane the mixture was heated another 40-50 minutes. The condensate in the trap, which consisted mainly of vinyl chloride, was distilled with the aid of a fractionating column. After a 2-fold distillation vinyl fluoride was obtained, boiling at -71° , -67° . The yield was 1 g, which was about 10%. The boiling point of the pure vinyl fluoride, isolated by repeated distillation, was -71 , -72° .

b) **Preparation of 1,1-fluorochloro-2-nitroethane.** A total amount of 10 g of vinyl fluoride and 16.5 g of nitrosyl chloride was placed in four thick-walled tubes cooled by a mixture of acetone and carbon dioxide. The tubes were sealed and left for 3 days at room temperature. The reaction mass acquired a dark green color. The cooled tubes were opened (increased pressure) and after the usual treatment their contents were fractionated first under

atmospheric pressure and then under vacuum. The following fractions were obtained: 1st, 77-113° (760 mm), 9.1 g; 2nd, 114-128° (760 mm), 8.9 g; and 3rd, 48-66° (15 mm), 5.1 g.

The fraction with b.p. 77-113° (760 mm) was a colorless liquid with the characteristic odor of chlorinated hydrocarbons. This fraction, which mainly consisted of 1,2-dichloro-1-fluoroethane (b.p. 73.7°) was not studied further. A second vacuum distillation of the other two fractions yielded a substance (8.7 g) which boiled at 50-65° (18 mm), the main bulk distilling at 54-57°.

Another distillation gave this substance in the pure state with b.p. 55.5° (18 mm). It was a colorless liquid, d_4^{20} 1.4961, n_D^{20} 1.4644 with a sharp odor. The substance is slightly soluble in water and is gradually hydrolyzed by water, chloride ions being found in the solution. It dissolves in 10% aqueous caustic soda giving an orange-yellow color, and gives a positive nitrol reaction for primary nitro groups.

6.679, 4.905 mg sub.: 4.769, 3.502 mg CO₂; 1.659, 1.109 mg H₂O. 4.315, 5.920 mg sub.: 0.407, 0.544 ml N₂ (23°, 24°, 746, 744 mm). 12.525, 6.080 mg sub.: 5.14, 2.521 ml 0.02 N AgNO₃. 0.1328 g sub.: 13.48 g benzene: Δt 0.375°. Found %: C 19.46, 19.47; H 2.78, 2.51; N 10.34, 10.68; Cl 29.15, 29.40. M 132.6. C₂H₃O₂NCIF. Calculated %: 18.8; H 2.37; N 10.98; Cl 27.8. M 127.5.

The above properties, analytical data, and the molecular weight of the substance indicate that it is 1,1-chlorofluoro-2-nitroethane. The yield (calculated from the weight of the fraction with b.p. 50-65° at 18 mm) was 54% based on the nitrosyl chloride used.

2. Reaction of 1,2-fluorochloroethylene with nitrosyl chloride. a) Preparation of 1-fluoro-1,2,2-trichloroethane and 1-chloro-2-fluoroethylene. Fluorochloroethane was prepared by the fluorination of symmetrical tetrachloroethane by antimony fluoride, by the method described by Swarts [3], but with some modifications. The reaction was carried out not in a copper apparatus, but in glass, and the catalyst used was antimony pentachloride activated by the addition of a small amount of bromine. These minor deviations from Swarts' method had the effect that the fluorination resulted mainly in the formation of fluorotrichloroethane and not of difluorodichloroethane, which is obtained in considerable amounts when Swarts' method is followed. The fluorochloroethylene was prepared strictly by the method given by Swarts.

b) Preparation of the acid chloride of fluorochloroacetoxyhydroxamic acid. 18.5 g of fluorochloroethylene and 13 g of nitrosyl chloride were placed in thick-walled glass tubes cooled by a mixture of acetone and carbon dioxide, and the tubes were then sealed. The mixture was held at room temperature (18-20°) during 72 hours, and the tubes were then cooled and opened. Increased pressure was noted during the opening. The color of the reaction mixture changed from dark red to brownish-red, and as the unreacted components evaporated from the opened tubes, to green. After removal of the unreacted components (8.5 g) the reaction mixture was subjected to vacuum distillation. When heated during the distillation in the distilling flask, the liquid became colorless. The distillate was divided into 3 fractions: 1st - 3.3 g of a colorless liquid boiling at 42-73° at 60 mm (this substance did not contain nitrogen and was not studied further); 2nd - 10 g of a colorless liquid, b.p. 75-85° at 60 mm; the 3rd fraction (3.4 g) distilled in the range 93-110°; the residue in the flask was 2.2 g. The 3rd fraction, as another distillation showed, mainly (2 g) consisted of the substance contained in the 2nd fraction.

Distillation of the fraction boiling at 75-85° at 60 mm yielded a colorless liquid with b.p. 76-78° at 60 mm, d_4^{20} 1.5749 and n_D^{20} 1.4472. The substance has a sharp odor, is soluble in water and the common organic solvents, and gives the hydroxamic reaction with ferric chloride. Aqueous solutions contain considerable amounts of chloride ions. The molecular weight, analytical data, and the properties of the substance indicate that it is the acid chloride of fluorochloroacetoxyhydroxamic acid. The yield of the acid chloride with b.p. 75-85° at 60 mm was about 45% calculated on the reacted nitrosyl chloride.

8.759, 6.444 mg sub.: 5.320, 3.943 mg CO₂; 0.960, 0.720 mg H₂O. 5.795, 5.970 mg sub.: 0.451, 0.431 ml N₂ (22°, 752 mm). 6.615, 5.975 mg sub.: 4.281, 3.90 ml 0.02 N AgNO₃. 0.13000 g sub.: 0.0810 g CaF₂. 0.2235 g sub.: 30.00 g benzene: Δt 0.254°. Found %: C 16.58, 16.69; H 1.27, 1.25; N 8.89, 9.04; Cl 45.9, 46.24; F 13.14. M 146.7. C₂H₂ONCl₂F. Calculated %: C 16.44; H 1.37; N 9.6; Cl 48.7; F 13.01. M 146.

The substance, like most acid chlorides of hydroxamic acids, decomposes on keeping, forming a colorless crystalline precipitate and evolving hydrogen chloride. With aniline it gives the anilide of phenylaminofluoroacetoxyhydroxamic acid.

To a solution of 1.6 g of the acid chloride of fluorochloroacetoxyhydroxamic acid in 10 ml of anhydrous ether a solution of 3.1 g of aniline in 10 ml of anhydrous ether was added in portions. The reaction was accompanied by

a small increase of temperature and the formation of a crystalline substance of a yellowish color. The anilide (1 g) with m.p. 156° was recrystallized from alcohol and dried in a vacuum desiccator.

It forms colorless shiny needles with m.p. 157°. The substance contains no chlorine and gives a positive reaction for fluorine.

6.255, 5.330 mg sub.: 15.100, 12.820 mg CO₂; 2.850, 2.280 mg H₂O. 5.593 mg sub.: 0.798 ml N₂ (24°, 760 mm). Found %: C 65.59, 65.81; H 4.79, 5.10; N 16.39. C₁₄H₁₄ONF. Calculated %: C 64.86; H 5.4; N 16.2.

3. Reaction of 1-fluoro-2,2-dichloroethylene with nitrosyl chloride. a) Preparation of fluorodichloroethylene. Fluorodichloroethylene was prepared by a method analogous to that described by Swarts [3].

70 g of fluorotrichloroethane was placed in an apparatus consisting of a round bottomed flask of 500 ml capacity fitted with a dropping funnel and connected to a fractionating column and a straight condenser. A solution of sodium amylate, prepared from 11.5 g of metallic sodium and 300 ml of isoamyl alcohol, was added by portions from the dropping funnel. The flask was heated carefully for several hours in such a way that the fluorodichloroethylene formed distilled off regularly. The yield of fluorodichloroethylene, with b.p. 37.5°, was 37 g.

b) Preparation of 1,1-fluorochloro-2,2,2-dichloronitroethane. 15 g of nitrosyl chloride (1.15 mole) and 22.5 g of dichlorofluoroethylene (1 mole) was sealed in each of two thick-walled tubes, with thorough cooling. The reaction mixture was left 7 days at room temperature (20-22°), when the liquid gradually darkened and finally attained a dark green color. When the cooled tubes were opened (increased pressure was noted), their contents were distilled under vacuum with the aid of a fractionating column. The unreacted components, about 35% of the original charge, distilled off first. Then, at 27-29° (50 mm) about 8 g of the nitroso compound formed in the reaction distilled in the form of a blue liquid. This was followed at 30-34° (50 mm) by several grams of a colorless liquid. Then an intermediate fraction (up to 64° at 33 mm) was obtained, and, at 64-70° (33 mm), about 25 g of fluorotrichloronitroethane in the form of a colorless liquid.

The nitroso compound was again distilled under vacuum with the aid of a fractionating column. It was observed that when the nitroso compound came into contact with rubber (stoppers and tubes) it immediately changed color, turning from a dark blue to a dirty-green liquid. The second distillation yielded 3 g of the nitroso compound in the form of a dark blue liquid with b.p. 28° at 8 mm. The nearly colorless residue from the distillation was fractionated together with the fraction boiling at 30-32° (30 mm); about 1 g of a colorless liquid with b.p. 30° (33 mm) or 53.5° (88 mm) was obtained. Elementary qualitative analysis of this substance showed that it contains chlorine but no nitrogen. This substance was not studied further. Analysis of the nitroso compound showed that it is not a single substance. It may be assumed that the nitroso compound was contaminated with a colorless nitrogen-free substance, which was probably fluorotetrachloroethane (b.p. 117° at 760 mm, according to Henne).

A second distillation of the fluorotrichloronitroethane fraction boiling at 64-70° (33 mm) gave pure fluorotrichloronitroethane (15 g). 1,1-Fluoro-2,2,2-dichloronitroethane boils at 68-69° (33 mm), d_4^{20} 1.677, n_D^{20} 1.399. The substance is insoluble in water and 10% caustic soda, does not decolorize aqueous permanganate solution, and does not liberate iodine from potassium iodide solution. It gives a characteristic reaction with dimethylaniline paper. The yield of fluorotrichloronitroethane boiling at 64-70° (33 mm) was 55% calculated on the reacted nitrosyl chloride.

6.979, 3.031 mg sub.: 3.343, 1.450 mg CO₂. 3.08, 3.815 mg sub.: 0.185, 0.226 ml N₂ (21°, 758 mm). 2.362, 3.541 mg sub.: 4.907, 7.358 mg AgCl. 0.1880 mg sub.: 9.0 ml 0.1 N AgNO₃. 0.1722 g sub.; 15.88 g benzene: Δt 0.295°. Found %: C 13.05, 13.06; N 6.86, 7.03; Cl 51.4, 51.41; F 9.04. M 189. C₂H₂Cl₃NO₂F. Calculated %: C 12.28; N 7.16; Cl 54.4; F 9.72. M 195.5.

4. Reaction of 1,1-difluoro-2-chloroethylene with nitrosyl chloride. a) Preparation of 1,1-difluoro-1,2,2-trichloroethane. The preparation of difluorotrichloroethane with the aid of antimony trifluoride was described by Henne [2]. Below is given a description of the preparation of difluorotrichloroethane with the aid of hydrogen fluoride.

An autoclave made of special steel, of 2 liters capacity, was charged with 1000 g of pentachloroethane (prepared by the fractionation of the chlorination products of dichloroethane), 800 g of anhydrous 99% hydrogen fluoride, and 500 g of antimony pentachloride. The contents of the autoclave were heated gradually, during 5 hours, up to 165°; the pressure was maintained at 40-45 atm. The excess pressure was released through a copper tube, as described for trifluorotrichloroethane (see below). At 165° the pressure increase became very slow, and the contents of the autoclave were distilled off during 20 minutes into the same bath containing ice. The heavy liquid obtained was washed first with a weak solution of alkali, then with water, and dried with calcium chloride. Yield 670 g. The mixture of fluorides was distilled with the aid of a fractionating column; a small amount of a low-boiling fraction

(40-72°) was followed at 72-74° by almost pure trichlorodifluoroethane in a yield of 520 g, and then by a high-boiling fraction up to 115°.

b) Preparation of 1,1-difluoro-2-chloroethylene. 80 g of zinc dust and 300 ml of ethyl alcohol was placed in a flask fitted with a reflux condenser, the upper end of which was connected to a trap cooled to -60°. The contents of the flask were heated to boiling, and 150 g of difluorotrichloroethane was gradually added during 2 hours through a capillary funnel. A further 60 g of zinc dust was then added to the flask, and the contents heated for 2 hours. The gaseous products evolved condensed in the trap in the form of a colorless liquid. When the reaction products were distilled over a fractionating column, a small amount (about 5 g) of a low-boiling liquid distilled over (at minus 28-26°), then dichloroethylene in a yield of 40 g distilled at -15.5°. As the boiling point of the difluorochloroethylene obtained did not agree with that given by Henne and Ladd [2] (b.p. -2.4°), the substance was analyzed and its molecular weight determined.

7.91 ml sub.: 3.98 ml 0.02 N AgNO₃. 11.51 ml sub. weighs 51.01 mg (13°, 736 mm). Found %: Cl 36.0. M 107.5. C₂HClF₂. Calculated %: Cl 35.8. M 98.46.

c) Preparation of 1,1-dichloro-2,2-difluoronitroethane and of the polymeric reaction products. 30 g of difluorochloroethylene and the molar proportion of nitrosyl chloride were placed in thick-walled glass tubes cooled to -50°, and the tubes were then sealed. At first the tubes were left in the light (300 W lamp) at 0° for 12 hours. At the end of this time distillation of the contents of one of the tubes showed that the components did not react in these conditions. The tubes were then kept at room temperature (18-20°) and opened after 70 hours. The brownish-green liquid which was formed was fractionally distilled under vacuum. The reaction liquid was a mixture difficult to separate by fractionation. During the first distillation, in order to avoid losses of low-boiling substances and decomposition of the reaction mass, the pressure was so regulated that the temperature within the liquid did not exceed 45°. By repeated distillations it proved possible to isolate an individual substance with b.p. 52° at 150 mm (2 g).

Under atmospheric pressure this substance distills without decomposition at 99°, and is a colorless liquid (d_4^{20} 1.597, n_D^{20} 1.3982) with a sharp odor, insoluble in water and miscible with most organic solvents.

The substance gives no color with ferric chloride, does not liberate iodine from potassium iodide solution, does not reduce aqueous permanganate solutions, and does not form chlorine ions on shaking with water. It does not dissolve when shaken with 10% caustic soda solution. On pyrolysis it gives off oxides of nitrogen, which give a characteristic color with Griess reagent.

5.560, 4.702 mg sub.: 2.800, 2.335 mg CO₂; 0.630, 0.510 mg H₂O. 4.702, 4.130 mg sub.: 0.294, 0.255 ml N₂ (14°, 738 mm). 11.750, 12.793 mg sub.: 6.53, 7.24 ml 0.02 N AgNO₃. 0.1658, 0.1489 g sub.: 18.2, 17.08 ml 0.1 N AgNO₃. 0.1612 g sub.: 20.10 g benzene: Δt 0.231°. Found %: C 13.75, 13.54; H 1.27, 1.21; N 8.11, 8.16; Cl 40.07, 40.13; F 19.6, 21.8. M 177.6. C₂HO₂NCl₂F₂. Calculated %: C 13.33; H 0.56; N 7.78; Cl 39.4; F 21.11. M 179.9.

The properties, molecular weight, and elementary analysis of the substance indicate that it is 1,1-dichloro-2,2,2-difluoronitroethane.

After distillation of the low-boiling fraction, the distillation flask contained the main bulk of the reaction products in the form of a pale yellow thick and viscous mass. Vacuum distillation of this mass yielded a high-boiling fraction which was much less viscous than the original mixture, and which distilled in the range 110-180° at 18 mm. The residue solidified completely on cooling. During a second distillation at the same pressure the liquid distilled completely in the range 110-150°. During the third distillation it was distilled up to 136°, the main bulk distilling at 132° (18 mm).

This compound is a fairly thick colorless liquid (d_4^{20} 1.751) with a faint odor. It is insoluble in water and when shaken with the latter gives only a slight amount of ionic chlorine. When shaken with 35-50% alkali solution, the substance reacts with evolution of heat, and large amounts of ionic chlorine appear in the aqueous solution. It gives no color with ferric chloride and does not decolorize permanganate; even on heating the substance reacts only slowly with permanganate, and does not add on bromine. Oxides of nitrogen are formed on pyrolysis. Distillation of the substance with zinc dust gives a colorless liquid, neutral to litmus, with an odor resembling that of acetamide.

Elementary analysis on the molecular weight of this substance showed that its composition is close to the empirical formula C₆HO₂N₂Cl₅F₄. It was not studied further.

2.170, 3.415 mg sub.: 1.470, 2.29 mg CO₂; 0.408, 0.530 mg H₂O. 7.425, 4.870 mg sub.: 0.451, 0.304 ml N₂ (21° 742 mm). 0.1087 0.1094 g sub.: 14.12, 13.93 ml 0.1 N AgNO₃. 0.5435, 0.5472 g sub.: 0.2517, 0.2626 g

CaF_2 • 0.2815 g sub.; 20.69 g benzene: Δt 0.170°. Found %: C 18.46, 18.29; H 1.6, 1.29; N 6.78, 6.90; Cl 46.09, 45.1; F 22.55, 23.31. M 409.5. $\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{Cl}_3\text{F}_4$. Calculated %: C 18.65; H 0.26; N 7.25; Cl 45.93; F 19.69. M 386.3.

5. Reaction of trifluorochloroethylene with nitrosyl chloride. a) Preparation of 1,1,2-trifluoro-1,2,2-trichloroethane. 1 kg of technical hexachloroethane, 450 g of antimony pentachloride, and 850 g of anhydrous hydrogen fluoride were placed in an autoclave of special steel, of 2 liters capacity.

The contents of the autoclave were gradually heated during 5 hours to 160°; the pressure was maintained at 45-50°. Excess pressure was released through a copper tube joined to the valve of the autoclave and with its other end immersed in an iron bath containing crushed ice. At 160°, when the pressure began to increase only very slowly, the contents of the autoclave were distilled off through the same tube into the bath with ice. The heavy liquid formed was separated from water, washed with 2% caustic soda solution and then with water, and dried with calcium chloride. Yield 710 g. The product was distilled with the aid of a fractionating column; the first fraction collected (150 g), which distilled at 45-49°, was 1,1,2-trichloro-1,2,2-trifluoroethane (boiling point of the pure substance is 47.7°); this was followed by an intermediate fraction, most of which distilled at 72-75° (this was difluorotrichloroethane, formed by the fluorination of pentachloroethane contained in the original hexachloroethane). At 90-92° a fraction (85 g) which was symmetrical difluorotetrachloroethane (boiling point of the pure substance is 92.8°) was collected.

b) Preparation of trifluorochloroethylene. 80 g of zinc dust and 30 ml of ethyl alcohol were placed in a flask fitted with a reflux condenser the upper end of which was joined to a trap cooled to -60°. 150 g of trifluorochloroethane was gradually added during 3 hours into the flask from a dropping funnel, a further 40 g of zinc dust was then added, the mixture was heated and kept for another hour with gentle boiling. The gaseous trifluorochloroethylene formed was condensed in the trap. The yield of the condensate was 85 g. The product was distilled over a fractionating column, and 57 g of trifluorochloroethylene with b.p. -27.5° (boiling point of the pure substance is -27.9°) was obtained.

c) Preparation of 1,1,1-difluorochloro-2,2,2-fluorochloronitroethane. 57 g of trifluorochloroethylene (1 mole) and 39 g (1.2 mole) of nitrosyl chloride were poured into thick-walled glass tubes with cooling. The mixture was held at room temperature (18-20°) during 96 hours, and the tubes were then cooled to -70° and opened. Increased pressure in the tubes was noted. The color of the reaction mixture changed from dark red to pale brown. The tubes were left at room temperature, when the greater part of the unreacted components (35% of the charge) evaporated. The remaining liquid was washed twice with water and dried with calcium chloride. The yield of the reaction products was 62 g. The liquid was distilled under vacuum to separate it from tarry impurities, the vapor being cooled by a mixture of acetone and carbon dioxide. Most of the substance distilled below 40° (90 mm). The residue was 6 g. The distillate was again distilled with the aid of a fractionating column without use of vacuum; the liquid was separated into 3 fractions. The 1st fraction (8.2 g) distilled at 45-52°; 13 g of the liquid distilled at 52-72°, and 21.5 g at 73-80°. The residue after distillation was 5 g. Vacuum distillation of the residue yielded a mixture (2 g) which boiled in the range 41-100° at 17 mm, and from which the individual substances could not be separated. The 45-52° fraction was trifluorotrichloroethane contaminated with a nitroso compound. In a second distillation the main bulk of it distilled at 47-48° as a heavy liquid slightly colored pale blue by a trace of nitroso compounds (d_4^{20} 1.61, n_D^{20} 1.3598).

A second distillation of the fraction which boiled at 52-72° showed that it was a mixture consisting chiefly of trifluorotrichloroethane (the total yield of which was 60%) and a small amount (about 3 g) of a liquid with b.p. 76-78°, which was in the boiling range of the 3rd fraction.

The 3rd fraction with b.p. 73-80° after two distillations yielded a substance with b.p. 77-78°, which was pure trifluorodichloronitroethane.

Trifluorodichloronitroethane is a colorless liquid (d_4^{20} 1.6202, n_D^{20} 1.3727), insoluble in water and miscible with most organic solvents. The substance is insoluble in aqueous caustic soda, and forms nitrogen oxides on pyrolysis. The yield was 65% calculated on the reacted nitrosyl chloride.

13.480, 7.010 mg sub.: 6.058, 3.197 mg CO_2 . 6.335, 5.977 mg sub.: 0.372, 0.352 ml N_2 (24°, 752 mm). 0.1241 g sub.: 12.64 ml 0.1 N AgNO_3 . 0.6342 g sub.: 0.3533 g CaF_2 . 0.1654 g sub.: 15.70 g benzene: Δt 0.280°. Found %: C 12.30, 12.45; N 6.68, 6.71; Cl 36.12; F 27.75. M 192.2. $\text{C}_2\text{O}_2\text{NCl}_2\text{F}_3$. Calculated %: C 12.12; N 7.07; Cl 35.82; F 28.79. M 198.

* Fluorine was determined by Bokemüller's method.

SUMMARY

1. The reactions of nitrosyl chloride with vinyl fluoride, 1,2-fluorochloroethylene, 1-fluoro-2,2-dichloroethylene, 1,1-difluoro-2-chloroethylene, and trifluorochloroethylene have been studied.

2. The following were prepared and investigated: 1,1-fluorochloro-2-nitroethane, 1,1-fluorochloro-2,2,2-dichloronitroethane, 1,1-dichloro-2,2,2-difluoronitroethane, 1,1,1-difluorochloro-2,2,2-fluorochloronitroethane, the acid chloride of fluorochloroacetylhydroxamic acid, and a substance with the composition $C_6H_2N_2Cl_3F_4$, formed in the reaction between difluorochloroethylene and nitrosyl chloride.

3. The addition of nitrosyl chloride to the above fluorine derivatives of ethylene proceeds in accordance with the polarities of the reacting bonds, so that the positive nitroso group is directed to the negatively polarized carbon atom linked by an ethylene bond, while the negative chlorine is directed to the oppositely polarized carbon atom.

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